A. P. HOWES
Publisher

M. D. REESER
Advertising Manager

AMERICAN DYESTUFF REPORTER

LOUIS A. OLNEY
Directing Editor

NORMAN A. JOHNSON
Managing Editor

DEVOTED TO THE INTERESTS OF TEXTILE CHEMISTRY
• BLEACHING • DYEING • FINISHING • PRINTING •
AND THE NECESSARY MECHANICAL EQUIPMENT

"Circulated Everywhere Textiles Are Processed"

Subscription Price: $5.00 per year; Canadian, $6.80; Foreign, $6.00. Fifty cents per copy

VOLUME 25 | JUNE 15, 1936 | NUMBER 12

CONTENTS OF THIS ISSUE

Contents of previous issues can be found by consulting the Industrial Arts Index at your library

General

Starch Viscosity 313
By Thomas H. Hart

The Nature of Cellulose (Concluded) 315
By E. Heuser

Washington News Letter 336
By Waldon Fawcett

New Products—Trade Notes 339

Proceedings of
American Association of Textile Chemists and Colorists

Preparation of Rayon Fabrics for Dyeing..... P320
A Paper By Hector C. Borghetty

Meeting, New York Section..... P322

Meeting, Southeastern Section P322

Meeting, Northern New England Section..... P322

Some Remarks on the Dyeing of Cellulose Acetate.. P323
A Paper By P. H. Stott

Mildewproofing and Waterproofing of Textile Fibers P326
A Paper By Samuel Lenher and George A. Slowinske

Applicants for Membership P331

Unemployment Register P332

Calendar of Coming Events P334

Editorial:

Japanese Dyestuffs 335

Official Publication of the American Association of Textile Chemists and Colorists

THE OBJECTS OF THIS ASSOCIATION ARE:

"To promote increase of knowledge of the application of dyes and chemicals in the Textile Industry.

"To encourage in any practicable ways research work on chemical processes and materials of importance to the Textile Industry.

"To establish for the members channels by which the interchange of professional knowledge among them may be increased."

Published Every Other Monday

HOWES PUBLISHING CO. ~ ~ 440 FOURTH AVE. ~ ~ NEW YORK

CLOSING DATE FOR ADVERTISING COPY . . . . . MONDAY PRECEDING ISSUANCE DATE

CALCONESE DIAZO BLACKS

CALCO DEVELOPER BON

(BETA OXY NAPHTHOIC ACID)

For Fibres of Acetate Origin

- CALCONESE DIAZO BLACK BD
- CALCONESE DIAZO BLACK GD
- CALCONESE DIAZO BLACK BWD
- CALCONESE DIAZO BLACK BDN

(Dustless)

Rich, bloomy shades.

Characteristics that record UNIFORM SUPERIORITY Under this Trademark

Calco

CALCONESE • COLORS •

THE CALCO CHEMICAL COMPANY • Inc.

• A Division of American Cyanamid Company

BOUND BROOK • NEW JERSEY

NEW YORK • BOSTON • PHILADELPHIA
PROVIDENCE • CHARLOTTE • CHICAGO

AMERICAN
DYESTUFF REPORTER

VOLUME 25 JUNE 15, 1936 NUMBER 12

Starch Viscosity

By THOMAS H. HART*

THERE is little doubt as to the fact that viscosity is the most important feature in the testing and examination of starches. This fact becomes most forcibly true when the examinations are confined to the testing of samples of the same type of starch. In such a case as this it also serves to show the money value of the starch by comparison of the known with the unknown. A sample showing the same viscosity as a known sample will have the same sizing value, equal adhesion, similar temperature of breakdown, be equal in actions with acids, alkalies or oxidizing agents, and will likewise require an equal amount of desizing agent to remove it. It will also require equal quantities of water and alkali to gelatinize it for the production of adhesives. Samples showing lower viscosities than a known sample will accordingly exhibit lower strength in the properties just mentioned and those with higher viscosities than a known sample will exhibit greater strength.

The testing and standardization of starch has presented many problems and difficulties. In many cases accurate work has been considered an impossibility. There are quite a number of cases where viscosities have varied on the same sample. Results of viscosity tests between laboratories have often varied and such results have become the source of considerable arguments due mainly to lack of uniformity and little actual knowledge on the subject. Each laboratory has had its own method of testing viscosity and has expressed its results in terms and units which have not been of an understandable nature to another laboratory.

A general survey of methods in use today for the determination of viscosity of starch and starch products may be divided into four general groups:

Method 1. Gelatinization of starch in either hot or cold water by means of an alkali, generally caustic soda, and then testing for viscosity. This method can only be used where the starch to be tested can be gelatinized by alkali as may be noted on Figure 1. Here we can see that such a method as this is excellent for use on tapioca flours and potato starches as well as several others but of no use whatsoever on the sagos. This method does not give any indication of how a starch will react on boiling in water. For instance if we compare sago starch in Figure 1 on which basis sago might be considered of low viscosity and a poor flour, to Table I showing a comparison of starches, on boiling in water, sago shows up fairly well being rated above corn starch which is lower than sago in Figure 1. The gelatinization of starches by alkalies will serve as a good indication for the color of the flour, providing the alkali used is clean, by noting the color of the solution in comparison with a known sample. The difficulties of the alkali gelatinization methods lie in the uncertain results due to the possibility of varying conditions:—for example Figure 1 shows the variation of viscosity by the length of time of reaction between the starch and the alkali at a constant temperature and a definite concentration of alkali, showing the more well-known starches. Figure 2 shows the variation of viscosity by

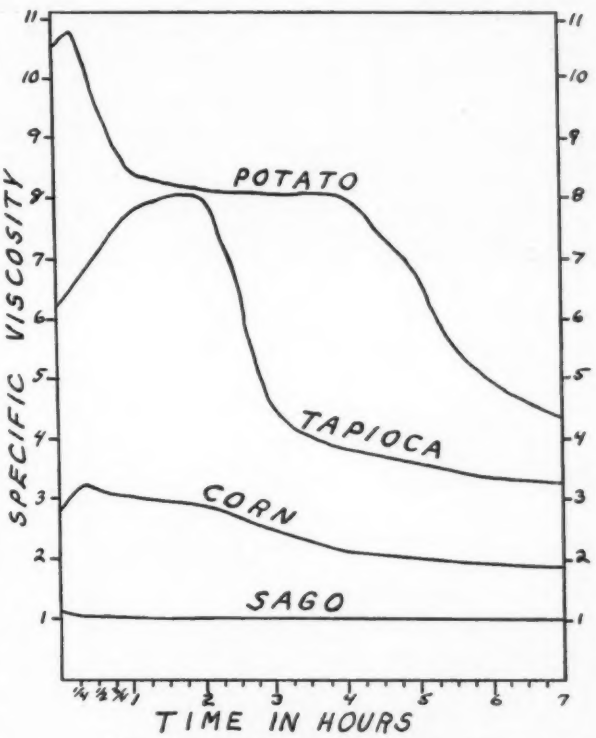

Figure 1.—Variation of Viscosity by Time.

*Chemist, T. B. Kane Mfg. Co., Philadelphia, Pa.

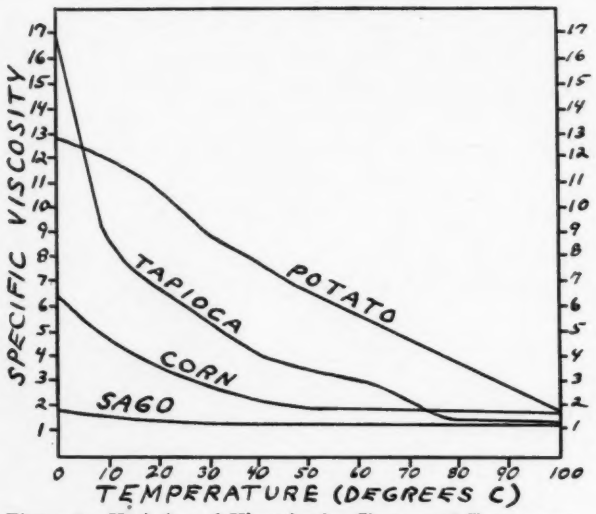

Figure 2.—Variation of Viscosity by Changes of Temperature.

TABLE I
Boiling Test

	Gelatinizing Temp. °C	*Specific Viscosity on Cooling to 50 °C.*
Corn	78-82	1.11
Tapioca	73-76	6.77
Sago	77	1.55
Potato	67-73	9.00

1 part starch to 20 parts water.

changes in temperature at a definite concentration of alkali and starch and a fixed time for testing. Here it must be also noted that on cooling a gelatinized solution of starch and water from a higher temperature, it will not thicken to same temperature that it would have been should the experiment be started at the temperature to which the gelatinized solution is cooled. Figure 3 shows the variation of viscosity due to changes in concentration of the alkali at a definite temperature and concentration of starch and a fixed time of testing.

Method 2. Starch is mixed with water using from 10-25 parts of water for one part of starch and heating until gelatinized over a steam bath and then testing for viscosity. In this method, time and temperature of conversion as well as type of agitation must be standardized to obtain good and accurate results. The temperature at which this gelatinized solution is tested is also an important factor.

Method 3. Starch added to water in the proportion of one part of starch to ten parts of water. This is the average amount of water required but it may be necessary to use more or less, depending on the variety of material being tested. This suspension of starch in water is then boiled using indirect heat. The resulting gelatinized solution is then cooled and tested for "Jelly-Strength" in some such apparatus as the Mac Michell Viscometer or the Bingham-Greene Plastometer.

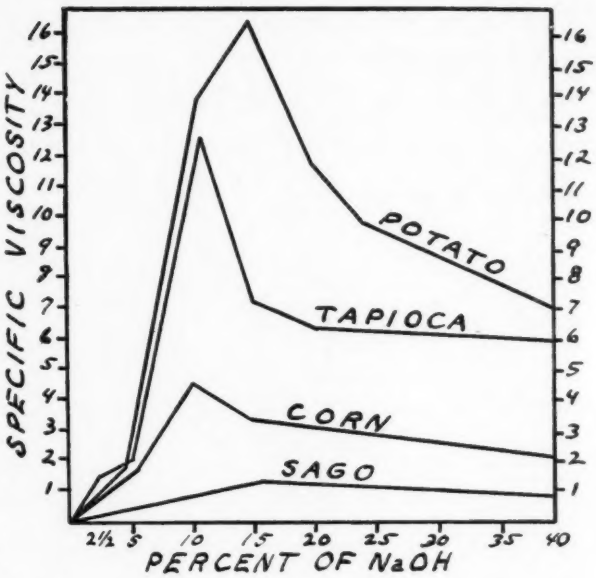

Figure 3.—Variation of Viscosity with Concentration of NaOH.

Method 4. A new method has been recently proposed using a mix of starch in water and cooking with live steam and agitating in a controlled manner. This method requires a special viscometer which is a modification of the Perkins Viscometer.

It should be noted that in all of the above results viscosities are expressed as specific viscosity. This is the relationship of the viscosity of the starch tested to water at equal conditions of temperature and volume. The ratio expressing the starch viscosity and the water viscosity will equal the specific viscosity or the number of times the starch is heavier or lighter than water under desired conditions. Many laboratories have made the mistake of reporting their results of viscosity as merely seconds, which to the next laboratory means absolutely nothing, but where specific viscosity is used, a definite standard is established which can be understood by all. The newer idea is to express all results in the terms of the absolute unit, the Centipoise. This unit is finding more and more use every day. It is possible to obtain standard solutions to time in any viscometer regardless of type so that by calculation of the time required for the standard solution to pass thru the viscometer, direct readings in centipoise may be obtained. The latest and one of the finest of viscometers is the Hoeppler type which operates on the principle of the falling ball and all readings are directly expressed in centipoises. Other types of viscometers used most generally are the Dudley Tube, also the Drucker and Ostwald Tubes, the Stormer, Saybolt, Engler and Perkins. All of these viscometers can be used to obtain specific viscosities and by use of standardized solutions, readings can be calculated directly to centipoises. For measurements of "jelly strength" as a form of viscosity as outlined under Method 3, a formula for conversion of

these results must be obtained by the user to convert the arbitrary units of that form of viscometer to give results in centipoises. Here again a standardized solution could be used to establish the readings directly in centipoises.

Although our knowledge of starches and their modified products is a study still in its infancy, it is becoming more and more generally realized that in regards to viscosities, definite and controlled conditions must be used and adhered to. The results of such tests must also be properly and accurately converted into understandable terms to be of real value for proper comparisons.

—♦♦—

The Nature of Cellulose

*An Historical Review**

By E. HEUSER**

(Concluded from March 9, 1936, issue)

IV. THE COLLOIDAL STRUCTURE OF CELLULOSE

ALTHOUGH reactions on cellulose which we must regard as typically colloidal were now and then studied rather early—for instance *Quincke* in 1861[1] found the fibers suspended in water through which an electrical current is conducted, to wander to the anode—classification of cellulose in its various forms as a colloid and more frequent studies on its colloidal structure go back only to the eighties of the last century. *Mills* and *Talkamie* (1883)[2] spoke about organic fiber "colloids," they studied the absorption on cellulose of acids from their solutions. *Mueller-Jacobs* (1885)[3] regarded the content of cells as being of colloidal nature; he also made observations on the diffusion of liquids and solutions through the cell membrance. *Cross* and *Bevan* (1886)[4] tried to explain the dyeing process on the basis of the colloidal structure of cellulose, and *Witt*[5], the best known fiber technologist of his time, classified all textile fibers as colloids (1888). It is true, colloid chemistry as a special branch of science was still young at that time; yet it appears strange that *Witt's* pronouncement did not cause the chemists to include cellulose, being in its organized structure no less important than the proteins, into the list of substances on which the chemistry of organic colloids has been methodically developed.

Thus, for a great number of years, we register comparatively only few investigations which would expressedly point out the colloidal structure of cellulose, most of them being concerned with the absorption of dyestuffs, until the first venture to deal with the colloidal properties of cellulose more systematically was made by *Cross* and *Bevan* in 1895[6]. Tempted to further studies by experiments which led them to endow cellulose with an "amphoteric activity" and with the ability to form "colloidal double salts" in cuprammonium and zinc chloride solution they made the behaviour of cellulose as a typical colloid in its manifold reactions a working hypothesis which they formulated as follows: "Cellulose . . . reacts as a labile complex of groups of varying dimensions representing a state of matter somewhat analogous to that of a solution of a saline electrolyte—that is, it reacts rather as a solution-aggregate than by a succession of molecular combinations."

Although Cross and Bevan tried to adhere to their working hypothesis in their manifold researches which followed, yet it appears as if, after all, they failed to systemize the experimental facts to such an extent as must be expected from any methodical treatment. Possibly they were aware of this insufficiency, for it appears as if they expected the professional colloid chemists to improve the situation. In commenting on Arthur Mueller's "Bibliography of the Colloids (1904)," they stated, "It is perhaps of interest to note that the cellulose is conspicuous by its absence from the extensive range of subjects and objects investigated."

Apart from Cross and Bevan's investigations, colloidal considerations still remained chiefly confined to studies on the dyeing properties of cellulose fibers, which resulted in the various dyeing hypotheses such as that of Zacharias (1900), of Justin-Mueller (1901) and of Pelet-Jolivet (1910).

This state of affairs caused *C. G. Schwalbe*[7], who surveyed the situation in a special chapter of his well-known book (1911) to wonder about the fact that, while the lack of systematical studies on fibers might have been excused by the lack at that time of methods for investigating such solid organic colloids, yet not even cellulose or its derivatives in solution had attracted enough interest in this respect. Nor had the so-called "Guignet-cellulose" of very interesting colloidal properties or Flechsig's "amyloid" been made the subject of systematical studies.

As regards the books on colloid chemistry the situation

* Paper prepared and partly read before the American Chemical Society (Cellulose Division) Tricentenary meeting in New York, April, 1935.

** Member of TAPPI, Manager, Research Department, Canadian International Paper Co., Hawkesbury, Ont.

is much the same. *Wolfgang Ostwald* (1917)[8] classifies cellulose due to its ability to swell and to the highly viscid nature of its solutions as belonging to the class of "emulsoids," but any methodical treatment of the colloidal properties of cellulose is missing.

This is also encountered in the books which deal with the chemistry or technology of cellulose in its various forms, published up to the year 1927. Although papers in which the colloidal character of cellulose is emphasized had been steadily increasing up to that time, and although they were considered at their proper places in various books, it was felt that there were still not sufficient data available to make a methodical treatment a successful undertaking. (Heuser, 1923 and 1927)[9].

In the meantime, special phenomena such as adsorption and swelling had received so much attention by specialists that the abundance of experimental data warranted such a methodical treatment. As a first although limited attempt in this direction we may regard the chapter entitled "Micellar Theorie and Swelling of Cellulose," written by Katz in C. Hess' book. (Chemie der Cellulose, 1928).

The most recent and quite successful attempt to treat the cellulose problem from the viewpoint of physical and particularly colloid chemistry was made by *Mark* in his book on "Physics and Chemistry of Cellulose" (1932)[10]. A shorter compilation of "The colloidal state of cellulose and its derivatives" was presented by *Duclaux*[11] before the international congress of chemistry in Liège, 1930.

The phenomena in which cellulose reveals its colloidal structure most obviously are (1) Adsorption, (2) Swelling, (3) Dissolution, and (4) Coagulation. The first two phenomena occur to a more or less pronounced extent in all reactions to which cellulose is submitted. Besides, they also are the initial steps which introduce the processes of peptisation and of dissolution. In addition to coagulation and regeneration the process of ageing in the presence of water or of alkalis reveals the colloidal nature of cellulose in manifold respects.

The phenomenon of adsorption has been studied with almost any substance, most intensively, however, with water, with dyestuffs, and with manifold types of electrolytes. In occupying ourselves with these phenomena we may remember that in cellulose we have to deal with a micellar system from which follows that the reactions which take place are of highly heterogeneous nature.

It is impossible to review in the time available the abundance of results which have been produced within the period under consideration, and I have confined myself to pointing out some more interesting facts and such on which a discussion—later on—appears desirable, while a more exhaustive review of the literature will appear in the printed paper.

Absorption of water on the fiber (i.e., on the external and internal surface), be it in equilibrium with atmospheric moisture or with water as in a fiber suspension or with water chemically bound, has an important bearing on many technical processes, such as conditioning of textiles with the reverse process of drying and the beating of cotton or wood pulp fibers as required for the manufacture of paper. The process of beating in recent years has been frequently made the object of scientific studies, particularly on the question as to whether the fibers, kept in contact with water for many hours under the cutting and fibrillating action of rotating knives, unite with water merely according to physical laws or combine with it chemically. At the time this phenomenon, which is called "hydration," started to interest scientists, the "chemical" hypothesis was fostered and "hydration" of cellulose fibers was compared with hydration as it occurs when inorganic salts form hydrates with water. (*Wurster,* 1903, *Beadle* 1908)[12]. However, *Strachan* (1925)[13], who investigated the phenomenon in a very interesting way, could find no indication for hydration in a chemical sense. Imbibition, which Strachan held responsible for the swollen state which the fibers attain, was found to increase considerably with fibrillation as it occurs under the action of the beater roll. The increase of strength observed on a sheet of paper made up from such "hydrated" fibers is explained solely by entanglement of the fibrillae[14].

Campbell (1930)[15] tried to measure the amount of hydration brought about by beating of a fiber-water suspension by determining the curve of vapor pressure against moisture content for the same fiber material before and after beating. But again there was no indication of a chemical combination between fiber and water.

Mark (1933)[16], in applying the theory of absorption, as developed by Adam, Encken, Polanyi, Langmuir and others, to very finely divided cellulose regenerated from a cuprammonium solution, calculated the surface area and the energy with which the water vapor molecules are fixed on the surface of the fiber. When beating fibers in a colloid mill he found the surface area to have increased enormously while the activity of the surface, that is, the forces which fix the water on the surface, have not changed. It is further assumed that it is through the secondary valencies of the oxygen atoms of the cellulose hydroxyls, exposed on the surface of the micellae, that the water molecules are fixed. The surface energy is distinctly increased, however, when acids or other chemical agents are added to the water, and Mark suggests that the chemical agents penetrate the micellae, thereby creating a passage for the water also. The latter then will attach itself to hydroxyls also inside the micella. Although the X-ray pattern of so "hydrated" cellulose, by the lack of any distinct change, does not indicate the existence of a true hydrate, Mark believes that it may well exist in the form of an addition compound similar to those which cellulose derivatives form with their solvents whose existence is indicated by their distinct X-ray pattern and which today are regarded as well defined through the investigations of Andress, Hess, Katz, Mathieu, Duclaux, Trillat and others.

More recent evidence as supplied by *Champetier* (1933)[17], also seems to point in the direction of a chemical combination between cellulose and water. Applying

Schreinemaker's method, Champetier found native cotton and ramie cellulose to add 1 molecule of water to 2 $C_6H_{10}O_5$ units whereas for mercerized cellulose the proportion 1 : 1 was found.

Thus it appears as if in the old controversy on what happens in the paper maker's beater, the hypothesis that "hydration" is a true hydration in the chemical sense, is again gaining stronger support and is about to restore the reputation of the early proponents of this hypothesis.

Although adsorption in many instances may be regarded the first process to take place whenever a cellulose surface comes in contact with water or other liquids, the phenomenon of *swelling* is closely related to it, and one may say that both phenomena are intimately interwoven, inasmuch as after initial adsorption has enacted the process of swelling on the surfaces between the micellae, this process in its turn may create access of the liquid to the inner parts of the micellae thus producing conditions for fresh or increased adsorption.

As mentioned before, our knowledge of the phenomenon of swelling of colloids, and particularly of cellulose in its various forms, has been much widened by the work carried out by Katz and his many co-operators. The standing of this knowledge at the beginning of the year 1928 and the development behind it is thoroughly reviewed in Katz' contribution to Hess' book on cellulose, and a more recent review was given by Katz in September, 1932, before the Faraday Society under the heading, "The Laws of Swelling," at a symposium at which "The Colloid Aspects of Textile Materials and Related Topics" were discussed[18].

As in other cases also here X-ray analysis has proven a great aid to the study of this phenomenon and has given a new impetus to research on the matter. Indeed, Katz regards it as the only experimental method which allows us "to penetrate into the *intimate* mechanism of swelling." As a matter of fact, X-ray analysis enables us to give a fairly satisfactory answer to the question of how and where the molecules of the liquid are deposited within the micellar structure of cellulose. A distinct change of the X-ray pattern permits us to state that the liquid has penetrated to the interior of the micella (intramicellar swelling). The lack of distinct changes of the pattern indicates that the molecules of the liquid have attached themselves only to the surfaces between the micellae (intermicellar swelling), although there exist cases where the unchanged X-ray pattern is not sufficient proof. For only a few layers of molecules might have been attacked. Moreover, the intermicellar substance might have been changed. But these changes would not alter the X-ray pattern.

Intramicellar swelling causes the dimensions of the basic cell to become enlarged according to a continuous function of the degree of swelling. If, however, a new diagram appears while the previous one loses in intensity, it is assumed that the liquid forms a chemical compound with the swelling substance. An example of the simultaneous occurrence of both is the action of strong caustic soda solution on cellulose.

Whereas X-ray analysis thus serves to clear up the geometric side of the swelling problem, a number of methods are available for studying the thermodynamics, and thus for answering the second question, i.e., what happens when a substance such as cellulose swells? Such methods are determination of the heat of swelling by means of a colorimeter and the energy of swelling, i.e., the affinity of the liquid for the solid of which information is obtained from determining the vapour pressure of the liquid in a partially swollen substance. The measurements on cellulose in various liquids and on its derivatives in their respective solvents allow us to assume that in the swelling process, chiefly at the beginning of it, forces of attraction of considerable magnitude are at work, and it appears as if the activity of such forces is the chief cause of the swelling phenomenon rather than the tendency of the molecules of the liquid to diffuse into the solid, a tendency which then may prevail when the maximum of swelling has been reached[19].

Whenever cellulose swells, pressure is developed, and to obtain an idea about its magnitude, *Katz*, in one of his publications[20] reminds us of the old Egyptians who "dynamited" rocks by filling a hole with carefully dried wood over which they poured water. The force developed by the swelling wood burst the rock. Swelling pressure may be measured by various methods, and it is interesting to note that Katz considered swelling pressure and osmotic pressure to be very much the same, seen from a thermodynamic standpoint[21].

This view, further extended to the similarity between swelling and capillarity (imbibition), has found confirmation in *Steinberger's*[22] thorough treatise on the thermodynamics of swelling (1934) in which it is suggested that "osmotic pressure is nothing but swelling pressure made evident by the external device of a semi-permeable membrane."

No doubt, through the various investigations of recent years the thermodynamics of swelling have been widely developed so that from its application to technical problems those cellulose industries which have to deal with swelling problems may derive much practical help.

Campbell[23], in his work on the beating action, directed attention to a factor which appears to have been not sufficiently considered in dealing with problems of swelling. This is the fact that cellulose is built up during plant growth in the presence of much water, the water occupying the spaces between the micellae and possibly within. This allows to conclude that the cellulose structure in this state is without strain. But on removing the water by evaporation a tension is developed which draws the structure more closely together, resulting in a deformation which introduces strain and which can only be relieved by the return of water. From this point of view the unstrained and swollen cellulose structure, as in the growing plant, is regarded as the normal state and not the strained and dry one, as was the old conception. The forces which cause deformation, i.e., the conversion from the normal into the

abnormal state, are found in the internal tension of the liquid. It appears as if this conception is liable to influence the attitude of scientists and technicians toward swelling problems, and its practical realization may lead to a better understanding of the various forms in which the phenomena of swelling and drying manifest themselves.

From both a scientific and a technical point of view absorption and swelling with electrolytes such as caustic soda solution, has received no less attention than have absorption and swelling in the presence of water. Since the investigation on alkali cellulose based upon the older studies by Gladstone, Vieweg, Karrer, and others was taken up again in 1924, also with the hydroxides of K, Li, Rb, and Cs[24] from which a hypothesis on swelling was developed[25], the controversy on the questions as to whether sodium hydroxide combines chemically with cellulose to form an "alcoholate" or an addition compound or whether simple absorption according to purely physical laws takes place, has not come to an end yet.

Only recently Bancroft (1935)[26] seems to close the issue with the statement: "There is no evidence of the existence in mass of any stoichiometric compound between sodium hydroxide and cellulose over the range of up to 20 per cent caustic soda."

That by applying other methods results have been obtained which point in the direction of well defined addition compounds has already been mentioned (*Champetier*[27]; also *Hess* and *Schwarzkopf*, 1933)[28]. X-ray analysis shows that below a concentration of the caustic soda solution of 9 per cent the hydroxide attaches itself only to the surface of the micellae, the X-ray diagram remains unchanged (Hess and Trogus, 1931)[29], and we deal with true absorption. With increasing concentration, however, the X-ray diagram changes indicating the formation of a chemical compound. It is generally assumed that the various alkali compounds do not contain water, an assumption which appears confirmed by Champetier's investigation, whereas *Neale*[30], who developed a somewhat different hypothesis on the reaction between cellulose and alkalis, formulates the compound with a certain stoichiometric amount of water.

Without assuming some type of chemical combination between alkali and cellulose an explanation of the viscose reaction with carbon-disulfide remains unsatisfactory since the latter reacts neither with cellulose nor with sodium hydroxide alone (Heuser and Schuster, 1926)[31].

The various methods of determining the degree of depolymerization have proven that of all means to bring cellulose into *solution*, cuprammonium, if applied under exclusion of oxygen and provided that the contact is short, is the one which achieves this aim without a measurable degradation. It is of all substances tried, still the solvent "par excellence." Not actually a solvent but a means of effectuating solution, for not the cellulose itself but a complex compound between cellulose and cuprammonium dissolves, or, more exactly, undergoes solvation with the solvent.

We remember that the rather complicated reactions which take place during this process have been fundamentally investigated by *Traube* (1922)[32] and later on became the chief subject of extended studies by *Hess* and his numerous co-operators[33]. Today[34], the hypothesis seems to be generally accepted that the complex cuprammonium ions $(Cu(NH_3)_4)^{++}$ enter the spaces between the micellae and attach themselves to the numerous hydroxyls available on the surfaces of the micellae. This process becomes visible through enormous swelling of the cellulose material. In accordance with the permutoid character of the reaction, the complex copper base also enters the interior of the micellae where there is another number of hydroxyls available. No doubt the regular arrangement of the hydroxyl groups in the crystal lattice causes the complex copper ions to attach themselves in a systematic manner as has been suggested in the case of other addition compounds of cellulose such as with water, alkalis, etc.

Since the viscosity of the solution is a measure for the degree of depolymerization of the cellulose used, it also is a means for giving an idea of the molecular weight of cellulose. The recognition that there exists a relation between molecular weight and viscosity is not new[35]. It may here be mentioned that *Berl* (1907) established this relation for the solution of cellulose nitrates in acetone and showed that severe pre-treatment of the cellulose results in low viscosity of the nitrate in solution[36]. Also *Ost* (1911)[37] expressed the opinion that the viscosity allows a conclusion as to the degree to which the cellulose had been degraded, and *Gibson* (1920)[38], using a more exact method of measurement, arrived at the same conclusion. However, while these investigations, with the exception of that on nitrocellulose, chiefly rendered a qualitative idea, *Staudinger*[39] developed the relation between viscosity and molecular weight on a quantitative basis, first on a series of further and further degraded cellulose acetates in acetone and thereafter on cellulose preparations, and on other derivatives, both of various degrees of depolymerization. The reliability of Staudinger's method for the determination of the molecular weight will be discussed by Dr. Kraemer in his paper.

It is interesting to note that the longer the chains when dissolved in cuprammonium, the more sensitive they are. This is evident for instance for the fact that the viscosity of a solution of native cellulose steadily decreases on standing whereas that of cellulose preparations regenerated from degraded acetates remains constant[40]. This sensitiveness of longer chains compared with shorter ones appears strange considering that the forces of cohesion increase additively with the length of the chain, and that both the longer and the shorter chains have been removed from the stabilized system in which they exist in the micella. An explanation is still lacking.

The very high viscosity of nitrocellulose solutions compared with other cellulose derivatives has led to the conception that these solutions contain the nitrocellulose in

(Continued on page 338)

PROCEEDINGS OF THE
American Association of Textile Chemists and Colorists

JUNE 15, 1936

Officers of the Association

WILLIAM H. CADY, *President*
U. S. Finishing Co., Providence, R. I.

A. R. THOMPSON, Jr.—ELMER C. BERTOLET, *Vice-Presidents*

WILLIAM R. MOORHOUSE, *Treasurer*
National Aniline & Chemical Co., Boston, Mass.

HAROLD C. CHAPIN, *Secretary*
Lowell Textile Institute, Lowell, Mass.

LOUIS A. OLNEY
President Emeritus and Chairman of the Research Committee
Lowell Textile Institute, Lowell, Mass.

Councilors-at-Large

JOSEPH F. X. HAROLD — HAROLD M. CHASE
DONALD H. POWERS — ARTHUR E. HIRST
CARL Z. DRAVES — HENRY F. HERRMANN

Councilors Representing Sections

BEN VERITY (Rhode Island) — EUGENE C. KNAEBLE (Philadelphia)
HANS MEYER (New York) — ELMER F. SMITH (Midwest)
ROLAND E. DERBY (N. New England) — R. S. WHEELER (South Central)
CHARLES B. ORDWAY (South Eastern) — CHARLES H. STONE (Piedmont)

Local Sections and Their Officers

Northern New England Section
Carl Z. Draves, Chairman, Ludlow Mfg. Associates, Ludlow, Mass.
John N. Dalton, Secretary, Pacific Mills, Worsted Division, Lawrence, Mass.

Rhode Island Section
John G. Masson, Chairman, Rosemont Mill, Woonsocket, R. I.
Raymond A. Pingree, Secretary, 7 Sayles Ave., Saylesville, R. I.

New York Section
George L. Baxter, Chairman, Bradford Dyeing Association, 40 Worth St., New York, N. Y.
P. J. Kennedy, Secretary, E. I. duPont de Nemours & Co., Inc. 61 Thomas St., New York, N. Y.

Philadelphia Section
Robert E. Sullivan, Chairman, Anchor Thread Co., Groveville, N. J.
R. W. Delaney, Secretary, National Aniline & Chemical Co., 200 S. Front St., Philadelphia, Pa.

Piedmont Section
Chester L. Eddy, Chairman, Renfrew Bleachery, Traveler's Rest, S. C.
Raphael E. Rupp, Secretary, Pacific Mills, Lyman, S. C.

South Central Section
Walter E. Hadley, Chairman, Standard Coosa Thatcher Co., Chattanooga, Tenn.
Murray B. Smith, Secretary, Standard Coosa Thatcher Co., Chattanooga, Tenn.

Midwest Section
Arthur T. Brainerd, Chairman, Ciba Co., 325 W. Huron St., Chicago, Ill.
Elias A. Johnson, Secretary, National Aniline & Chemical Co., 357 W. Erie St., Chicago, Ill.

South-Eastern Section
C. A. Jones, Chairman, Georgia School of Technology, Atlanta, Ga.
Robert H. Harris, Secretary, Spalding Knitting Mills, Griffin, Ga.

Lowell Textile Institute Student Section
Herbert A. Wormwood, Chairman; Henry S. Anthony, Secretary

North Carolina State College Student Section
A. E. Shumate, Chairman; J. W. Furr, Secretary

Members should notify the **Secretary** immediately of all address changes

Standard Wash Fastness Samples

Cotton, Wool, Silk

The standard samples which have been in preparation for some time by the Sub-Committees on Fastness to Washing of Dyed Cotton and Dyed wool are now ready for distribution, and the original standard silk sample cards have been revised to correspond with the new system of classification first introduced in the 1934 Year Book.

These standards have all been carefully dyed with the dyestuffs and according to the dyeing methods recommended in the 1934 Year Book and each set includes a dyeing representing each of the different classes of fastness.

With these sample dyeings for reference it will be possible to accurately grade the fastness to washing of any dyed cotton, wool, or silk fabrics, by comparing them with the standards after subjection to the standard washing tests as approved by the Association.

The A.A.T.C.C. is now prepared to furnish these three sets of washing standards for $3.00 or $1.00 per individual set which is to cover the cost of preparation.

All inquiries concerning these washing standards should be addressed to the Chairman of the Research Committee.

LOUIS A. OLNEY,
LOWELL TEXTILE INSTITUTE,
LOWELL, MASSACHUSETTS.

Preparation of

Rayon Fabrics for Dyeing*

By HECTOR C. BORGHETTY†

IN recent years we have witnessed the steady and increasingly successful adoption of fabrics made with synthetic fibers. Parallel to this the necessity has arisen to process these fabrics by means which would permit the economical handling of the large and increasing volume of business. The variety of rayon fabrics made nowadays is such that it is advisable this evening to limit the field to one of the main groups.

Let us consider cloths of flat construction, namely. taffetas, twills, lining cloths, satins and similar, both of rayon and acetate rayon.

Let us also take occasion to consider the possibilities of processing these fabrics by *continuous methods* and see how present equipment and means of prepare fit in with this type of processing.

In the matter of continuity, present day methods of rayon processing leave much to be desired. In fact, there is a constant endeavor to accelerate the speed of operations throughout the plant where frequently the drawback of the lack of continuity is felt. The existing methods of continuous prepare, which are those used for cotton, cannot be generally considered as suitable for the delicate rayon fiber. This fiber would be damaged were it subjected to drastic chemical treatments in rope form. Nor, furthermore, would such treatments be necessary, because as we are well aware, rayon fabrics do not contain the impurities of cotton grey cloths. The impurities present in rayon grey goods are merely those which have been added to facilitate weaving operations.

To process rayon fabrics in a continuous way, it therefore, is necessary to use scouring solutions capable of eliminating the sizing ingredients *without* damaging the fiber and this must be accomplished with machinery which will not subject the fabrics to fraying or creasing. In other words, it will be advisable to make use of open width machines, namely, open width soapers, padders, jigs, vacuum extractors, etc. In connection with the impurities present in rayon grey goods it has always been the earnest wish of the finishing plant personnel to be informed by the grey mill just what type of sizing ingredients have been used. It has always been *hoped* that these ingredients be readily removable. Both this wish and this hope are very often disappointed. To many it has never been quite clear why some grey mills persist in adding all kinds of insoluble unknowns without paying the least attention to the fact that the finisher is placed in the position of removing them without destroying the cloth. In view of the fact that this condition exists it must be countered by analysis of the ingredients present in the cloth of the various grey mills and by conforming scouring operations so as to take care of the type of sizing present, as efficiently as possible. Of course, in the average finishing plant one becomes accustomed to the fact that certain grey mills generally use certain compounds.

Tests conducted on grey goods from various mills generally reveal that the sizing used is either a gelatin or starch base. Thus, steeping of the grey goods in a solution of an enzyme capable of digesting these products will be our first operation in the majority of cases.

When the goods contain starch sizings a diastatic enzyme is necessary. In case of gelatin or casein sizings it will be found strongly advisable, particularly in case of acetate fabrics, to use a protease. There are on the market enzymes which answer these respective uses satisfactorily. They are all buffered to the proper hydrogen-ion concentration so as to function under the best conditions. There are some enzymes which contain both diastatic and proteolytic components and can therefore be used for solubilizing both starches and gelatin sizes. In some instances it will be found possible to omit the preliminary steeping entirely—such would be the case when sizing ingredients of the dextrine type have been used. These are soluble without a preliminary malting action.

There still persists the fallacy of using mineral acids as desizing agents. These are out of the question because the acid will weaken the filling threads before it has a chance to solubilize the size in the warp threads.

The operation of malting is carried out either on the jig (for small runs) or on the pad. The correct concentration, generally between 1-6% of enzyme must be used at its optimum temperature. Once impregnated, the cloth must be allowed to stand batched up for at least 2 hours, although a longer period is better.

A thorough impregnation is essential and care should be taken that the roll contains an excess of liquid so as to allow the sizing ingredients to swell and then be acted upon by the solubilizing enzyme. Good impregnation is generally easy to obtain on the jig where it is always possible to give an extra end. On the pad, however, it often

*Presented at meeting, Rhode Island Section, January 24, 1936.
†Chief Plant Chemist, Aspinook Company.

happens that the amount of desizing solution present in the cloth is insufficient to perform its function. Better impregnation is assured by using an impregnating machine instead of a pad, thus giving several dips through the solution before squeezing out the excess. Soft squeeze rolls will also be found advisable as they permit a longer contact. Precautionary measures to observe are:

1. Cover the sides and ends of the padded rolls with a cloth dampened with the solution of enzyme—otherwise these parts will dry out quickly and the enzyme becomes inactive. This precaution eliminates one of the causes of side shaded dyeings.

2. Change the position of the roll frequently to avoid accumulation of liquid on the lower part of the roll which would cause loss of solution.

Once solubilized, the sizing ingredients can be readily removed by scouring.

Scouring may be accomplished either on the jig or in a continuous manner.

The jig is used for acetate fabrics and all others that have a tendency to wrinkle. For a jig scouring usually 6-8 ends at 180-200° F, in the presence of about ½% soap solution and final rinsing is sufficient. For acetate fabrics (mixtures of acetate and rayon are usually processed as acetate) the temperature should not be maintained much above 180° F. else a partial saponification takes place which causes a great deal of inconvenience in subsequent dyeing. Saponification of acetate fabrics takes place much more readily if alkalies are present and particularly if the pH value is above 10.

This fact leads many to attempt scouring in a neutral bath such as is obtained by the use of sulfonated alcohols and similar scouring agents. Practical trials, however, show that in scouring goods containing digested gelatin sizes, a more efficacious scouring action is had at pH 8-9 than at the neutral point.

There are cases, and unfortunately very many, in which the scouring becomes far more complicated and expensive than a mere washing for an hour or so. This is in reference to sightening colors of the wrong type being used in the grey goods. In many instances not only is the warp intensely colored, but the entire goods are "plastered" with signs and impressions (night and day stampings, change of size, experiment marks, etc.) For the removal of such products it often becomes necessary to use a stripping agent as a supplementary operation after the scouring. Hydrosulfite and caustic are generally the most efficacious.

For continuous scouring the present day open width soaping machine is used. This machine consists of a series of compartments containing scouring liquors and rinse waters. One of the essential points is that the machine be equipped with feed-tanks in which the scouring solutions are made up and controlled.

Although the time factor is short compared to that on the jig, it can be somewhat compensated for by using stronger solutions at higher temperatures. The final rinse can be given with hot water. Caustic is sometimes used in one of the compartments and its swelling action on the fiber appears to help level the dyeing properties.

Drying after preparing seems also to assist in obtaining more level dyeing. One must not expect to eliminate the well known inconvenience of streaky dyeing by merely giving a caustic treatment to the fabric and a drying on cans. The subject of dyeing streaky rayon is not on discussion tonight and it involves the characteristics of the dyestuff, its rate of aggregation, absorption and diffusion, etc. Nevertheless, in preparing fabrics it is only fair to eliminate unevenness in warp sizing, when possible, so as to send on to the dyehouse scoured goods which have an even chance of dyeing up satisfactorily.

For the bleaching of rayon fabrics there are two main bleaching agents—chlorine and peroxide. Chlorine, although more economical, does not possess the flexibility of peroxide bleaching methods. It is furthermore not suitable for acetate bleaching as it tends to impart a rather disagreeable odor to the fiber. Chlorine is generally applied in a similar manner as used for cotton, by impregnating the fabric with a solution of a hypochlorite at about ½-1° Tw., allowing to stand a few hours, then giving an antichlor.

Peroxide bleaching, although it gives at times a somewhat harsher and duller fabric has the decided advantage of producing a better and more endurable white. Its main advantage consists in the speed of operation and in the fact that it can be used simultaneously as a scour and bleach. It also opens up a good field for semi-continuous and continuous bleaching and can be used very successfully for acetate rayon. For jig work the average procedure is to run the desized goods through a solution of peroxide and silicate, then heat to 160° F. and maintain at this temperature until bleaching has taken place.

When it is desirable to scour and bleach at the same time this can be effected by running the *dry* grey goods through the bleach liquor and soap and thus obtaining a thorough impregation. The temperature is then raised and bleaching takes place gradually. After the bleaching agent is exhausted, it will be possible to add more soap and continue to scour until such impurities as sightening colors are completely eliminated. This method can be adapted to continuous work by impregnating the grey goods with a strong solution of bleach liquor and allowing to stand cold for several hours until the bleaching action is completed, then scouring in the continuous machine. When the cloth is in a well scoured condition successful dyeing depends on the proper selectivity of the dyestuffs and any troubles that occur should be traced to this operation and not usually to bad rayons, or faulty grey goods.

DISCUSSION

Q. How about using the dry can for drying rayon?

A. Perfectly all right. If you use the dry cans just before finishing, you get a harsh feel. They are not recommended therefore for the last operation.

Q. Suppose you get "C" quality rayon, what are you going to do?

A. There is not much to be done about such rayon excepting to use all precautionary measures possible.

Q. What particularly harmful ingredients have you found in rayon sizing?

A. We have found about everything, waxes, linseed oil and even iron salts. Linseed oil, I should say, is generally not suitable.

Q. The general constituents of a rayon size should be comparatively simple chemically?

A. Yes. Some mills are successful in using a dextrine size. It is very easy to remove. If all the mills did that, the problem would be quite simple.

Q. Do you find more difficulty in removing gelatin sizes than starch sizes?

A. I separated the sizes into two groups, because you require two enzymes. When dealing with a very tightly woven piece of goods, the starch is more difficult to remove than gelatin.

Q. Have you had any experience with casein?

A. It acts in the same way as gelatin. Of course, if the casein contains a calcium salt, it might cause some trouble.

Q. Can you give a quick test for gelatin size?

A. You can dye the gelatin with a basic color. The best way is to use the tannic acid test: Precipitate the gelatin with tannic acid.

Q. Can you tell us how strong the caustic should be in boiling off rayon?

A. It depends on the construction of the cloth and the type of finish you want to give. 3-4% is advisable and up to 5% the concentration is still all right. Use the caustic along with one of the sulfonated alcohols.

Q. In talking about impurities in the cloth coming from the warp or filling, are there any impurities coming from the yarn itself?

A. There might be impurities in some of the oils used to soften the yarn, but the rayon manufacturers are usually careful to use an oil which is readily removed.

Q. Do they use neatsfoot oil for this?

A. No, not generally. Mixtures of mineral oils are used.

MEETING, NEW YORK SECTION

THE regular monthly meeting of the New York Section was held on Friday evening, April 24, 1936, at the Swiss Chalet, Rochelle Park, N. J.

Ormand W. Clark of Umans Brothers spoke on "Problems in the Dyeing of Cotton and Linen Fabrics with Fast Colors".

Henry F. Herrmann, Chairman of the Outing Committee, stated that definite arrangements for the Annual Outing had been made with the North Jersey Country Club, Paterson, N. J., for Friday, June 26th.

Chairman Ephraim Freedman cautioned the members against a New York photographic organization which in soliciting business had given the impression that it had authorization from the Association. Usually this was by telephone.

Attendance was approximately one hundred.

Respectfully submitted,

P. J. KENNEDY, *Secretary.*

MEETING, SOUTHEASTERN SECTION

THE Spring meeting of the Southeastern Section was held at the Thomas Hotel in Auburn, Alabama, on April 25, 1936, at 7 P.M.

Professor Robinson of the Alabama Polytechnic Institute spoke on "Termites and Their Control".

Sidney M. Edelstein, Research Associate of this Association, spoke on "Mercerization Research, Its Value and Practical Application".

Donald H. Powers of Rohm & Haas Co., Inc., spoke on "Permanent Finishes on Textile Fabrics".

This Section was happy to have President Cady as its guest.

Respectfully submitted,

ROBERT H. HARRIS, *Secretary.*

MEETING, NORTHERN NEW ENGLAND SECTION

A MEETING of the Northern New England Section was held at the Andover Country Club, Andover, Mass., on Friday evening, May 15. At this meeting the nomination and election of officers for 1936-1937 was held. Henry D. Grimes as Chairman of the Nominating Committee reported the following list of officers:

Chairman, Carl Z. Draves; Secretary, John N. Dalton; Treasurer, John H. Grady; Sectional Committee, (for 2 years), Harry F. Finlay, Edwin A. Buthmann; Councilor, Roland E. Derby.

The above nominations were moved and accepted by the meeting and the secretary was instructed to cast one vote for their election.

Edward Weber, Chairman of the 1936 Outing Committee, reported that this year's outing would be held on Friday, June 12, at the Nashua Country Club, Nashua, N. H.

Following the business meeting, a four-reel sound movie showing the manufacture and uses of Enduro stainless steel was presented by the Republic Steel Corp. George Hinkle of this company presented a very interesting and instructive talk and answered many questions regarding the use of the various Enduro stainless steels in the textile industry. About 50 members were present at the dinner and meeting. Respectfully submitted,

JOHN N. DALTON, *Secretary.*

Some Remarks on the Dyeing of Cellulose Acetate*

By P. H. STOTT†

DURING the last ten years, cellulose acetate has achieved considerable importance as a textile fiber. The estimated annual consumption has increased to about 55 million pounds. It is only natural that much thought should have been given to the problem of successfully dyeing it. In the first place no theory of dyeing has been sufficiently exploited to give chemists and dyers a clear insight into the principles involved. With the advent of cellulose acetate, it became apparent that the new synthetic fiber had characteristics all its own and that very few of the known dyestuffs could be satisfactorily applied to it. Any fiber must be capable of absorbing color to enhance its sales value and consequently it became necessary to synthesize colors differing chemically from existing standards. Without definite knowledge of the dyeing mechanics of the new fiber this problem was an acute one. For a time acetate was considered of little importance because of the difficulties of dyeing it. As the new products were developed it was perhaps not surprising that they possessed two characteristics not common to well defined dyestuff behavior. First, they were as a class insoluble in water and second, they were not susceptible to chemical treatment to make them soluble, such as the vat and sulfur colors, and in this condition have affinity for cellulose acetate. It was apparent from the start, therefore, that here was an entirely new conception of the art of dyeing, namely to apply insoluble color to fiber with no possibility of chemical treatment to improve its affinity. At present two theories of dyeing cellulose acetate appear to have possibilities for further exploitation. First—the solid solution theory—that is an actual dissolving of the color in highly dispersed condition by the fiber and second —a chemical union between the acetyl groups and certain groups in the color. It seems to be a fact that such colors containing free amido groups uninfluenced by sulfonic acid groups have outstanding affinity for cellulose acetate. It is not proposed to discuss these possible theories, as sufficient evidence is not yet available to prove or disprove either of them. We are mainly concerned with the fact that it is impossible to successfully dye acetate unless the colors used are in a highly dispersed condition. Of late years physicists have devoted much time to studies of particle size, atomic activity and electronic theories in all branches of science and as you know some startling discoveries have been made which have led to a clearer understanding of many problems. These developments have found their places in the textile industry in such fields as fiber construction—starch and size application—dyeing and many others not necessary to mention here. There probably is a relation between these facts and the dyeing of cellulose acetate particularly if the solid solution theory has any stable basis.

To attempt to dye a textile fiber with a solid dyestuff at once suggests trouble. All dyers know the danger of dyestuff agglomerates in the dye bath even when using a water soluble color. The possibilities of obtaining spotty or streaky dyeings when using an insoluble color would therefore be increased, particularly when a marked affinity for color by cloth exists as is the case generally with cellulose acetate. It has been the aim of dyestuff manufacturers to supply colors for acetate in as fine a condition of subdivision as possible, either by chemical or mechanical means or both; and many colors are now available in such a highly dispersed form as to be almost soluble. It must, however, never be forgotten that actually the majority of colors are not soluble—they are in effect emulsions and as such can be broken down. This point brings us to the preparation of the color prior to dyeing. Speaking very generally prolonged or vigorous boiling; long standing; the addition of inorganic salts; and a suddenly increased dilution of the concentrated emulsion are agencies which will tend to cause separation. The dyer, therefore is well advised not to boil acetate colors vigorously. A safer technique is to heat the water separately, pour it slowly over the color, stirring the latter into a smooth thin paste before completing the dilution. The suspension thus prepared should be used as soon as possible. It is not advisable to make stock solutions and use them over an indefinite period. On entering the dyebath the emulsion is rapidly diluted, probably in the ratio of 1:250 and therefore the preparation of the dye liquor to maintain the stability of the dispersion is of great importance. Soap, sulfonated oils and similar products are in general use for this purpose and as dyeing assistants. These products possess emulsifying properties and help materially to maintain the dispersion of color. They can be augmented by the use of the sulfated higher fatty alcohols which not only are powerful emulsifying agents

*Paper read before the R. I. Section, Jan. 24, 1936.
†E. I. du Pont de Nemours & Co., Inc.

but also have the additional advantage of being less sensitive to the formation of insoluble alkaline earth soaps if the water available is at all hard. The formation of such insoluble soaps is at times accompanied by occlusion of color and causes spots on the goods which are very difficult if not impossible to remove. They can also be responsible for resist marks if they are carried over from the boil-off and a careful study of local conditions is necessary to obtain the best dye liquor and corrective measures.

While the use of inorganic salts such as Glauber's salt and common salt plays no part in the dyeing of all acetate fabrics they must be used in dyeing fabrics containing rayon or cotton to exhaust the colors used for the latter. In dyeing such fabrics as crepes, therefore, it is considered good practice not to add the direct colors at the outset but to run the goods for about 15 minutes with the acetate colors alone and give them opportunity to be picked up by the fiber. Direct colors can then be added and finally the salt. By following this method all danger of breaking down the dispersion of the acetate colors by the addition of the salt is avoided. If the dispersion is broken it will lead to cloudy dyeings, poor penetration due to excess surface color absorption and the possibility of crocking.

In a talk of this length it is hardly possible to cover all phases of acetate dyeing on all types of materials in any great detail. Flat goods such as satins, taffetas, twills are jig dyed; crepes and similar fabrics on the over-head reel machine and pile fabrics on the star reel or spider. We also have to consider whether the fabric to be dyed is woven of bright or delustered yarn. If the former a dyeing temperature of about 170-180° F. is considered the maximum owing to the danger of saponifying the acetate; if the latter, temperatures can be carried to a practical boil. Most dull acetate yarns are delustered by incorporating a pigment in the solution of the acetate before spinning and the delusterant is stable but has some tendency to resist penetration of color. Naturally, the delustered yarn when dyed gives an appearance of lack of depth but we believe this is not due to lower affinity for color but merely because the delusterant acts more or less similarly to an opaque pigment as used in compounding paints. Acetate does not absorb as much water as rayon, actually only about 10-20 per cent of its weight and therefore is more or less water proof by comparison. Its tensile strength when wet is only about 50 per cent of its dry strength, consequently careful handling in the wet state is necessary.

By far the greatest yardage of acetate fabrics being dyed today are crepes for dress goods. The construction of these fabrics varies greatly and new constructions are constantly appearing. This season has seen the introduction of Oatmeal, Friendship, Ganza and others in addition to the older 2x2 and 4x4 constructions. The boiling off of these materials has been described by the previous speaker, so we can take up the question of dyeing and finishing from that point. We have two fibers to consider—the acetate warp and rayon filling. The latter being a more or less highly twisted yarn presents difficulties of penetration covered as it is by the acetate warp. The crepeing effect of the rayon naturally causes a drawing together of the warp and in heavy crepes penetration of this is also difficult. You are familiar with the dyeing apparatus used so we will not take time to describe it. As in the dyeing of all other fabrics, color selection plays an important part in results obtained. Probably one of the main difficulties in dyeing acetate is the selection of colors with an even exhaustion rate over a temperature range of 120° F. to 190° F. As research discloses new dyestuffs and the number of available colors is augmented this problem will be aided, but it has existed and still does to a certain extent. I have in mind at the moment three dyestuffs which show the following relative exhaust speeds taking 160° F. as a basis for comparison.

	120°	140°	160°	190°
A. Orange	70	90	100	110
B. Red	20	80	100	200
C. Blue	20	60	100	100

A brown made from such a combination would be very difficult to control particularly because of the much increased affinity of the red element at 190° F.

Another and much better combination would be

A. Orange	35	60	100	100
B. Red	30	70	100	110
C. Blue	20	60	100	100

In such a combination the shade would be brown throughout and there would be little danger of the red element feeding on towards the end and causing shady dyeings through surface absorption, as in the first combination. Penetration with the first combination would probably not be good for the same reason. As far as we know at present the acetate colors do not seem to be susceptible to additions to the dyebath to retard or facilitate exhaustion as other classes of colors are. Direct colors dyed on cotton or rayon can be retarded or accelerated in exhaust and the same statement pertains to vat colors. In these cases, however, we are dealing with dyestuffs in solution as distinct from acetate colors which as pointed out are in suspension. It seems logical therefore to conclude that even more careful attention should be given to color selection in the latter case. The question is frequently asked "What can we do to increase penetration then and still get production at reasonable cost?" Some of you practical men may know more answers to that question than I do. The composition of the dyeing liquor is undoubtedly one of the answers. Acetate is not very absorbent and anything that can be added to the dyebath to increase its absorbency will help in penetration of color. Ideas vary greatly on the nature of these assistants. Much depends on water conditions and naturally on the type of

material being processed. The sulfated fatty alcohols have been found of value in this respect. Two typical formulas for a dye liquor for a box containing 20 pieces of crepe could be given if only for purposes of comparison.

8 lbs. Olive oil soap	6 lbs. Olive oil soap
12 oz. "Gardinol" WA Flakes	3 lbs. Sulfonated castor oil
1 lb. Soda ash	8 oz. Brilliant "Avirol" L-144
	1 lb. Hexameta phosphate of soda

Penetration can also be materially helped by prolonged treatment of the goods at temperatures near the boil. It is realized that this is not too satisfactory a solution of the problem owing to loss of production, possible tendering of fabric and chafing, but it is often the only recourse on certain fabrics. It may be of interest to note here that many acetate colors have a tendency to "migrate" under certain conditions such as heating near the boil, steaming and in some instances just by contact. This is probably a reason why prolonged heating increases penetration. Incidentally this tendency has been the source of some difficulties encountered, particularly that of sublimation and marking off in steaming and published information on fastness properties of acetate colors now usually contains some reference to this feature.

The question of penetration of the rayon in crepes also deserves referring to. Such colors as have high affinity for rayon such as Black BH, the Purpurines and others are probably best avoided in favor of the more slowly exhausting colors such as Fast Scarlet 4BA, Black E and Blue RW types. It will be found however, that the dyeing assistants used for the acetate will generally help the rayon to be penetrated and not too much difficulty should be anticipated in this connection.

FLAT GOODS

Those colors possessing good affinity at a temperature of 160° F. are best suited for flat goods as these are almost invariably jig dyed and are in contact with the dye liquor for a comparatively brief period. The general remarks made so far are applicable to the dyeing of flat goods also. Taffetas and similar fabrics are difficult to penetrate due to the tightness of weave and sometimes they are woven with a bright warp and delustered filling which adds to the problem. About the only recourse is the use of dyeing assistants adapted to local conditions.

Cellulose acetate has found considerable use in the preparation of novelty fabrics in which it is woven with rayon, cotton or silk in pattern weaves. It is also used largely in the manufacture of the cheaper styles of men's hosiery. The fact that it is resistant to dyestuffs used for rayon, cotton and to a certain extent, silk, obviously is a great asset as patterns can be woven and stocked in the grey and then be dyed to order at short notice in any shade combinations desired. This fact makes the stocking of dyed yarns unnecessary. There are many colors available which dye rayon and leave acetate unstained or practically so. Some examples of these are available for those who care to inspect them. Any slight staining of either acetate or rayon can be corrected by soaping or treatment in weak hydrosulfite solution. A good black on acetate with white rayon can be made by using one of the developed blacks for acetate and clearing the rayon *before* diazotizing by treatment with weak hydrosulfite. This is more satisfactory than clearing after development as the coupled product is more resistant to the action of hydrosulfite.

There is quite some difference of opinion on the question of the correct drying temperature for acetates. It is our experience that a temperature of about 160-180° is best to avoid any harshening of the fabric and subsequent difficulties in finishing.

FINISHING

For heavy crepes it is advisable to use a softening agent in the last rinse. Brilliant "Avirol" L-144 has been found of value in a concentration of about 4 oz. per 100 gallons. This product has definite affinity for acetate and retains its softening action.

For finishing through the "quetsch" this product in conjunction with sulfonated olive oil produces a good finish and for crepes a dulling agent such as "Neotone" T is generally used. A typical formula.

10 oz. Sulfonated Olive Oil	)
	)
10 oz. Brilliant "Avirol" L-144	) Per 16 gals. at 120° F.
	)
4 oz. "Neotone" T	)

Brilliant "Avirol" L-168 Paste gives a fuller and somewhat oilier hand than L-144 and is liked by many finishers. One advantage of these sulfated fatty alcohols is that they had no tendency to become rancid on storing.

There are many additional points which can be touched on, but we believe that in a meeting of this kind any further time available would best be used for purposes of discussion and we will be glad to try to answer any specific questions that may be raised.

DISCUSSION

Q. How does the decrease in strength of wet rayon over dry rayon compare with acetate?

A. Wet rayon decreases about 55 per cent and wet acetate about 45 per cent.

Q. Has anything been accomplished in overcoming the breaking down of blues on acetates when stored?

A. That's a good question, but I don't know the answer. I don't know just why the blues do break down. It is possible to imitate the results in several ways. There are two ways I can quote. You can imitate the results by treating the blue with a solution of Nitrous Acid. It seems that those dyes which contain amino groups are more susceptible than others, and the blues are particularly susceptible. Also, you can expose the dyes to the fumes of burnt coal gas. In England they had an epidemic of complaints following a period of unusually damp and foggy

weather. The gases in the atmosphere were increased by such fogs and also more coal gas was burnt, and they got the idea that there might be some relation between the production of burnt coal gas and shading on the edges of rolls of cloth. The results can be imitated in the laboratory in similar manner.

Q. What is the best way to strip acetate colors from the fiber?

A. I don't know that they can be successfully stripped except by prolonged treatment with hydrosulfite and frequent soaping.

Q. What can be done to increase fastness to rubbing of dull acetates in dark shades?

A. Any particular shades in mind? You mean direct dyes?

Q. Yes, in navies and browns, for example.

A. There is a relation between the fastness to rubbing and the efficiency of the dispersion of your dye,—the smaller the particle size, the more efficient the emulsion and the less tendency to crock. Surface dyeing colors also increase this tendency.

Q. Any reason why deep colors, like navy, for example, when they get to a certain shade don't seem to get any darker no matter how much color you add?

A. It is at least partly due to the pigmentation of the rayon. The pigment has the effect of showing through.

Mildewproofing and Waterproofing

of Textile Fibers*

By SAMUEL LENHER† and GEORGE A. SLOWINSKE†

TEXTILE fibers are valuable, and their value is greater when the fibers' life is lengthened. Fabrics are subject to destructive attack apart from normal wear. One frequent attack is by mildew. When this attack can be prevented or delayed the life of the fabric is prolonged and its value to the consumer is increased. Textiles are utilitarian, and the longer the purpose of the textile is fulfilled, the more valuable the textile is to the user. When a fabric is treated especially to render it water-repellent it is satisfactory only as long as the water-repellent property persists. Any increase in the durability of this property increases the value of the fabric.

This paper considers processes to give lasting protection from mildew attack and to give durable water-repellency to textiles. These two processes do not change the character of the textile, that is the color, odor, appearance, and finish, to any marked degree but add the properties of mildew resistance and water-repellency.

MILDEWPROOFING

Mildew or mildew damage is an all too common occurrence in the cotton and cotton textile industry. It has been estimated[1] that the losses in raw cotton in the United States from such damage is between twenty-five and seventy-five millions of dollars per year. However, until less than two decades ago no systematic efforts were made to prevent these losses. Since 1920 extended researches have been made in the study of the microbiology of textiles with particular reference to methods of prevention of damage by microbiological action.

Mildew has been described as a "fungal growth producing an undesirable effect—usually a discoloration—on cloth or yarn"[2]. More particularly mildew damage is caused by the action of micro-organisms or parasitical plants which have a world wide distribution. Of these many micro-organisms the cotton industry is mainly concerned with the fungi or true fungi (classified botanically as the Eumycetes). The predominant genera of the Eumycetes are the Aspergillus, Penicillium, Fusarium, Mucorales, and Fungi Imperfecti. One investigator[2] states that the genera Aspergillus and Penicillium are the most abundant and that of the two, the genus Penicillium is the more common in England because it tends to grow at lower temperatures. Another authority[3] found that in America the genus Aspergillus was the predominant genus in the south while the genera Penicillium and Mucorales were the predominant ones in the northern states.

A fungus colony consists of minute threads (the main plant bodies, or hyphae) forming a sort of network (the mycelium). On branches of the network are minute bodies called spores. It is by means of these spores that the fungi are distributed and propagated. Fungi obtain nutrient from such complex substances as cellulose,

* Presented at meeting, South Central Section, Feb. 22, 1936.

† Technical Laboratory, Organic Chemicals Department, E. I. du Pont de Nemours & Co., Inc.

[1] Procter, B. E. and Chace, W. G. in "Textile Research—A Survey of Progress," U. S. Institute for Textile Research, Inc., p. 75 (1932).

[2] Galloway, L. D., J. Text. Inst., *21*, T277 (1930).

[3] Wakeman, S. A., Soil Science, *3*, 567 (1917).

starches, sugars and proteins. As a consequence they can readily grow on textile materials provided other conditions are favorable. The chief essentials in addition to the presence of nutrient are moisture and warmth.

Fabrics suffering fungal attack may become discolored and musty in odor and in extreme cases may be tendered or destroyed. The observed color in a fungus colony is due to the presence of colored mycelium, colored spores, or to by-products formed during the growth of the fungus colony. Most fungi produce enzymes which can act on cellulose to break it down into simpler soluble products capable of being assimilated. Such action necessarily results in tendering or even destruction of the cellulose fiber.

Two remedies are available to prevent mildew damage. The growth and reproduction of fungi may be prevented by keeping their environment unsuitable, or antiseptics (fungicides) capable of destroying the fungi may be used. The first method is open to obvious disadvantages. Fungi grow best under conditions of moisture and temperature to which practically all cotton is subjected at one time or another from the cotton boll to the finished fabric. Various investigators[2, 4, 5] have shown that cotton cloth containing less than 8-9% moisture will support little or no mildew growth but that mildew can develop rapidly on fabrics containing slightly higher moisture contents (10-13%). It also has been reported that a black species of the genus Aspergillus grew best at a temperature of 98° F., a white species of Aspergillus grew best at 77° F., and a green species of Penicillium grew best at 80° F. Maintenance of the moisture content of cotton at all times below 8% and maintenance of the temperature sufficiently high or low to retard fungal growth is nearly impossible. Prevention of fungal growth only part of the time by such means is of little value. When conditions are unsuitable the spores remain dormant. As soon as warmth and moisture are encountered the spores germinate and if suitable nutrient such as cellulose, starches, and proteins are present growth of the fungi takes place.

The second method suggested, the use of antiseptics is a logical method. Many different agents have been suggested in the literature and many different ones have been used. Such materials as zinc chloride, phenol (carbolic acid), cresol, salicylic acid, formaldehyde and thymol have been extensively used. All of these chemicals show serious disadvantages. Zinc chloride is only effective at very high concentration. Because of its hygroscopicity it imparts a damp feel to the fabric. Because of its hydrolizing action the danger of serious tendering is always present. The phenolic compounds possess objectionable odors; most of them are volatile in steam and consequently losses occur in the size box. Salicylic acid is a good antiseptic in acid solution but its toxicity is destroyed by the presence of even small amounts of alkali. Therefore, it cannot be used in sizing mixtures which are alkaline, nor can it be applied to goods which are slightly alkaline in reaction from previous treatments such as mercerizing or kier boiling, unless the alkalinity is first counteracted. Thymol is too expensive to use in most cases. Formaldehyde is objectionable because of its high volatility and irritating vapor.

Antiseptics are known, however, which do not possess the more obvious disadvantages as hygroscopicity, high price, objectionable odor, color and volatility. Most of these do not adequately protect fabrics which are subjected to the repeated wetting, drying and mechanical action such as takes place during weathering. Canvas and duck materials which are subjected to weathering frequently develop mildew growth after use even though they were treated with a fungicidal agent before use. During rain storms the material is either leached out or mechanically removed. As a consequence the material develops mildew growth when it becomes wet.

In the present work the fungicidal agent employed was salicylanilide. This product was selected as the result of research carried out at the Shirley Institute[6] in England, in which over 160 compounds including inorganic salts, organo-mercury compounds and organic compounds were extensively tested. The use of salicylanilide as a mildew preventative is the subject of British Patent No. 323,579 and United States Patent No. 1,873,365. Salicylanilide is marketed under the registered name of *Shirlan*.

Shirlan or salicylanilide itself is a white, stable, odorless solid. It is sparingly soluble in water; 100 grams of water at 25° C. dissolve 0.005 gram, and 100 grams of water at 100° C. dissolve 0.08 gram[6]. Salicylanilide is an efficient agent for use in preventing the growth of those fungi which attack textile materials.

Products based on salicylanilide have been developed which can be applied readily to textile materials at any manufacturing stage and which meet a wide variety of requirements. These products are Shirlan Extra, Shirlan D and Shirlan A.

Shirlan Extra is salicylanilide of commercial grade. It finds its chief use in mildewproofing heavy cotton fabrics which are subjected to weathering and is admirably suited for application to wool yarns and fabrics. It is applied from ammoniacal solution. A 2 per cent stock solution may be prepared by adding 2 parts of Shirlan Extra to 89 parts of water, heating to 160° F. and adding, with stirring, 9 parts of a commercial (28-30 per cent) ammonia solution. Baths suitable for treating textile materials may be prepared from the stock solution by the addition of water or water containing a small amount of ammonia. The yarn or fabric should be impregnated with the treat-

[4] Armstead and Harland, Shirley Institute Mem., *2*, 339 (1923) or J. Text. Inst., *14*, T475 (1923).
[5] Bright, T. B., Morris, L. E., Summers, F., Shirley Institute Mem., *3*, 295 (1924) or J. Text. Inst., *15*, T547 (1924).
[6] Fargher, R. G., Galloway, L. D., and Probert, M. E., J. Text. Inst., *21*, T245 (1930).

ing solution and then dried. The ammonia evaporates on drying, and leaves the insoluble Shirlan uniformly dispersed throughout the fibers and threads. Shirlan Extra also is readily soluble in such solvents as ethyl alcohol, methyl alcohol, acetone and "Hexalin" (technical cyclohexanol), and may be applied from these solvents if convenient.

Shirlan D is salicylanilide in a readily dispersible powder form. It is 60 per cent as strong as Shirlan Extra. It finds its chief uses in mildewproofing yarns or fabrics where a simple method of application is required. Shirlan D is admirably suited for incorporation in starch sizing or finishing mixtures.

Shirlan A is a special aqueous dispersion based on salicylanilide. It is 30 per cent as strong as Shirlan Extra. It has been developed for use with Aridex WP, the waterproofing dispersion which will be described later. A method of treatment whereby textile materials are rendered both mildew-proof and water-resistant is ideal for certain classes of work. Awnings, tents and sail cloth which are subjected to weathering during use may be enhanced in value by treating with both Shirlan A and Aridex WP. The two products are compatible with each other and can be applied in a single bath. Both products contain a dispersing agent which fixes the active mildewproofing and waterproofing ingredients to the fibers. The dispersing agent has film forming and fixative properties which give unusual fastness properties to inert materials such as salicylanilide and waxes when applied to fibers.

In practice the requirements of each particular case will dictate which of the Shirlan types should be used. Adequate protection is obtained in many cases by a simple treatment in a dispersion of Shirlan D; in other cases treatment in an ammoniacal solution of Shirlan Extra will be more effective. In cases where the maximum protection is required for fabrics exposed to the elements during use the single bath treatment involving Shirlan A and Aridex WP is required.

Experience, based on the results of both laboratory and large scale commercial tests, has shown that the amount of Shirlan necessary to inhibit mildew growth differs in individual cases. This is caused by the fact that the effective concentration required is influenced markedly by the presence of sizing materials, by the conditions of storage or use, and the locale. Such materials as starches, dextrins, tallow and glue aid mildew development by furnishing nutrient for the mildews or mold fungi. Different types of fungi are prevalent in different sections and their sensitivity to antiseptics varies. In a series of rice culture tests[7] it was found that no one fungicidal agent was equally effective in preventing the growth of different mold organisms. Consequently for economical application of Shirlan the necessary concentration of Shirlan Extra, Shirlan D and Shirlan A should be determined by trial in each individual case.

We have developed an accelerated laboratory mildew-resistance test which has proven of value. In this accelerated mildew-resistance test fabric samples before and after treatment with Shirlan are inoculated with five different species of fungi and are stored in an atmosphere saturated with water vapor at a temperature of 77-90° F. The samples are examined for mildew growth after two months' time. Previous work demonstrated that samples of fabrics which do not develop growth in two months' time under such favorable conditions will not develop growth under most conditions encountered by fabrics in actual use. In inoculating the fabrics a suspension of the spores (and mycelium) taken from cultures of the different species is made and atomized onto the fabrics. The cultures are purchased from the American Type Culture Collection, 637 South Wood Street, Chicago, Illinois. The cultures consist of pure strains of the species, Aspergillus Niger, Aspergillus Glaucus, Aspergillus Fumigatus, Penicillium Digitatum and Penicillium Brevicaule.

Our tests have shown that the following range of concentrations for Shirlan Extra, Shirlan D and Shirlan A cover practically all requirements provided a thorough penetration of the textile material is obtained.

TABLE I

Treating Bath Concentration Ranges for Shirlan Types When Textiles Absorb Their Own Weight of Liquor

Product	*Treating Bath Concentration in Per Cent*
Shirlan Extra	0.06 — 0.15
Shirlan D	0.10 — 0.25
Shirlan A (plus Aridex WP)	0.10 — 0.50

The following tabulation gives concentrations of Shirlan Extra, Shirlan D and Shirlan A which were found effective in actual tests. In each case the particular fabric before treatment was found to be susceptible to mildew growth.

TABLE II

Treating Bath Concentrations of Shirlan Types Found Effective in Actual Trials

Fabric Treated	*Shirlan Type Used*	*Treating Bath Concentration in Per Cent*
COTTON		
Duck (unbleached, undyed)	Shirlan D	0.24
Toweling (bleached, undyed)	Shirlan D	0.10
64/68 Sheeting (bleached, undyed, commercially finished)	Shirlan D	0.20
Twine (unbleached, undyed)	Shirlan D*	0.66
Yarn (unbleached, undyed)	Shirlan D*	0.25
Yarn (bleached, undyed)	Shirlan D*	0.24
Duck (8 oz., unbleached, undyed)	Shirlan A**	0.50
Duck (8 oz., mineral dyed)	Shirlan A**	0.25
Duck (13.65 oz., unbleached, undyed	Shirlan A**	1.00
Duck (8.42 oz., unbleached, undyed)	Shirlan A**	0.25
Duck (sulfur dyed)	Shirlan A**	0.25
Duck (sulfur dyed)	Shirlan A**	1.00
WOOL		
Oiled wool piece goods—(4.4% grease content)	Shirlan Extra	0.0625-0.125

* The Shirlan D was incorporated in heavy starch sizing mixes.
** The Shirlan A was used in conjunction with Aridex WP in a one bath operation.

[7] Tests conducted by Dr. A. L. Flenner of the Jackson Laboratory, E. I. du Pont de Nemours & Co.

In interpreting the data in Table II it should be noted that the different fabrics absorbed different amounts of the treating liquor. In some cases the fabric absorbed only 50-60 per cent of its own weight of treating liquor. The general treating bath concentration limits given in Table I are based on the assumption that the textile being treated will absorb about 100 per cent of its own weight of treating liquor.

In the following table are given the results of an experiment showing the weather resistance of Shirlan D and Shirlan A and combinations of Shirlan A and Aridex WP when applied to a cotton fabric. Samples of a cotton drill were treated with (a) various concentrations of Shirlan D, (b) various concentrations of Shirlan A, and (c) various concentrations of Shirlan A in conjunction with Aridex WP. The treated samples were cut into two parts each. One part of each treated sample and a sample of untreated fabric were tested immediately for resistance to mildew growth by means of our accelerated test. The second part of each treated sample and a sample of untreated fabric were exposed to the weather for two months and then tested for resistance to mildew growth by means of the same accelerated test. The results illustrate the permanency of protection against mildew growth imparted to the fabric treated with Shirlan A and Aridex WP. The results also show that Aridex WP itself rendered the fabric resistant to mildew growth. This property of Aridex WP has been observed in a number of other instances although it is not recommended for use alone as a mildewproofing agent.

TABLE III

Weather Resistance of Shirlan Types Applied to a Cotton Fabric

Composition of Treating Bath— Concentration in Per Cent			**Mildew Resistance of Fabric*	
Shirlan D **	*Shirlan A* **	*Aridex WP*	*Before Weathering*	*After Weathering*
0.06			P	NP
0.12			P	NP
0.24			P	P
	0.12		P	NP
	0.24		P	NP
	0.48		P	P
		2.5	P	PP
	0.12	2.5	P	P
	0.24	2.5	P	P
	0.48	2.5	P	P
Control, untreated			NP	NP

* The code "P" means that the sample was protected against mildew growth or that it developed no growth in the accelerated test.
The code "PP" means that the sample was partially protected against mildew growth or that it developed a slight mildew growth in the test.
The code "NP" means that the sample was not protected or that it developed pronounced mildew growth in the test.
** Shirlan D is twice as strong as Shirlan A.

WATERPROOFING

Waterproofing by simple treatment in a single bath followed by drying at an elevated temperature is carried out with the product Aridex WP. This stable wax emulsion is the product of our research laboratories. It is a white, waxy emulsion which can be diluted readily with hot or cold, neutral or slightly acid water. It is suitable for treating natural silk, viscose rayon, cellulose acetate, linen, wool, cotton, and grass textiles. The effect imparted to fabrics by Aridex WP is most accurately described as a water-resistant or water-repellent effect. Aridex WP, at effective dilutions, does not coat fabrics, i.e., does not fill up the interstices between threads and prevent the passage of air or of water under pressure. It does not impart any color or odor to fabrics. It does not change the essential physical characteristics, such as appearance and handle to any marked degree. It does not alter the fastness to light of dyed textiles, except in the cases of a few dyes. It merely adds the property of water-repellency or water-resistance to textiles.

Aridex WP contains a dispersing agent with film forming and fixative properties which imparts unusual fastness to the active waxy ingredient when applied to textiles. The dispersing agent in Aridex WP is not attacked by soap; consequently fabrics treated with Aridex WP are unusually fast to washing, dry cleaning and weathering in comparison with other products of the same general type. In a practical test, automobile top fabrics treated with Aridex WP withstood four months' weathering without showing any material decrease in water-repellency. In another outdoor exposure test with Aridex WP treated natural silk, wool and cotton fabrics it was found that Aridex WP had no observable effect on the natural weather resistance of cotton and wool and actually increased the resistance to weathering, i.e., resistance to loss of tensile strength, of natural silk.

The application of Aridex WP to textiles is essentially simple. All that is necessary is to impregnate the textile in a diluted bath of Aridex WP under suitable conditions, squeeze out the excess treating liquor, and dry at a high temperature. Practical experience has shown that all types of textiles can be processed with Aridex WP on the usual equipment in textile mills. The best results are obtained when reasonable care is observed in each step of the process. These steps are briefly:—

Preparation of Aridex WP Treating Baths

Aridex WP is a slightly acid product and is not stable in the presence of alkalies. Consequently the water used for dilution must be neutral or preferably slightly acid (pH of about 4.5-6.0). Dilute acetic acid may be used for acidification of the dilution water. As with all wax emulsions Aridex WP should be diluted by adding the dilution water to it slowly, with stirring. Aridex WP is not stable in the presence of alkaline salt solutions, sulfates, soaps, sulfonated oils and alcohol sulfates, and consequently these should not be added to diluted Aridex WP treating baths.

Treatment of Textiles in Aridex WP Baths

Fabrics before treatment should be free of any residual alkali remaining from previous operations. Care should be taken that the treating bath is maintained in a slightly

acid condition during its entire use. Temperatures up to 180° F. may be used.

Drying of Textiles Treated with Aridex WP

After impregnation, textiles should be dried at as high a temperature as possible. High temperature drying melts the wax in Aridex WP with the formation of a more water-repellent film. It also sets the fixing agent in Aridex WP more firmly, giving a water-repellent effect which is more resistant to removal by washing, dry cleaning or weathering.

Aridex WP may be applied in a continuous process by immersion padding or in a batch process in a piece dye kettle. The type of fabric dictates which type of process is the most economical. Experience has shown that cotton, viscose rayon and cellulose acetate fabrics are best treated in a continuous process and that wool and natural silk are best treated in a batch process. It has been found that with wool and pure silk textiles very high exhausts of Aridex WP from treating baths occur, depending somewhat on the particular conditions prevailing, such as the treating bath concentration, the temperature and the condition of the fabric. This high affinity of Aridex WP for wool and pure silk makes the application of Aridex WP to these materials in a standing bath very economical.

The results of a laboratory experiment in treating viscose rayon, cotton, wool and natural silk should be of interest in showing the relative magnitudes of the exhausts of Aridex WP from treating baths onto these textiles. Samples of viscose rayon, cotton, wool and natural silk were treated for 15 minutes at 120° F. in 0.1 per cent and 1.0 per cent emulsions of Aridex WP. The liquor fabric ratio used was 25 to 1. The percentage exhausts obtained were determined by comparison of the emulsions after use with standard emulsions of known concentration (Table IV.)

An additional experiment showed that increasing the temperature to 175° F. increased the exhaust obtainable on all four classes of fabrics.

The concentrations of Aridex WP and the particular procedures required for different textiles vary widely with (a) the type of fabric, (b) the initial absorbency of the fabric, and (c) the requirements. In Table V data on actual successful applications of Aridex WP to different viscose rayon, cellulose acetate, cotton, wool and natural silk fabrics are given. The data cover both labo-

TABLE V
Application of Aridex WP to Textiles

Type of Textile	*Per Cent Aridex WP in Bath*	*Type of Process*	*Scale of Process*	*Application Details*
COTTON				
Umbrella cloth (dyed)	6	Continuous	Commercial	Padder (176°F.) with and without Schreiner Calender (after drying)
Duck (dyed)	5	Continuous	Laboratory	Padder (170-180°F.), hand iron (direct contact)
Uncut pile fabric (bleached)	5.	Continuous	Semi-Commercial	Padder (180°F.), drying cans, ironing mangle
8 oz. awning cloth (dyed)	4	Continuous	Commercial	Padder (170°F.)
Corduroy	5	Continuous	Commercial	Padder (two passages)
Shower curtain (bleached)	5.2	Continuous	Commercial	Padder (170-185°F.), with and without Calender (after drying)
Broadcloth (bleached)	8	Continuous	Laboratory	Padder (170°F.), hand iron (direct contact)
Suiting fabric (dyed).	8	Continuous	Commercial	Padder
Napped fabric (bleached)	6.7	Continuous	Laboratory	Padder (130-140°F.), hand iron (direct contact)
Automobile top fabric..	5	Continuous	Commercial	
VISCOSE RAYON				
Crepe	6.7	Continuous	Laboratory	Padder (130-140°F.), hand iron (between cloth)
Dress goods fabric...	0.7	Continuous	Commercial	Padder (quetsch)
Umbrella fabric	6 and 8	Continuous	Laboratory	Padder (140-150°F.), hand iron (between cloth)
Umbrella fabric (cellulose acetate stripe).	4.2	Continuous	Commercial	Padder (165°F.)
Taffeta	2.5	Continuous	Commercial	Padder (65°F.), Palmer Machine
Taffeta	6	Continuous	Commercial	Padder
CELLULOSE ACETATE				
Dress goods fabric....	0.7	Continuous	Commercial	Padder (quetsch)
Taffeta	3 and 4.5	Continuous	Commercial	Padder (quetsch, 120°F.), frame, Palmer Machine
NATURAL SILK				
Umbrella cloth (viscose rayon stripe)..	6	Continuous	Laboratory	Padder (130-140°F.), hand iron (between cloth)
Hosiery (different grades)	0.3-1.2	Batch	Commercial	Dyeing machine (90-110°F., 5-10 min.) 30-40 lbs. hose to 100 gal. liquor (6.25-20% Aridex WP on weight of silk)
WOOL				
Outer clothing fabric..	3	Batch	Commercial	Fulling Machine (110°F., 20 min.), 75 lbs. wool to 50 gal. liquor (16.7% Aridex WP on weight of wool)
Outer clothing fabric..	1	Batch	Laboratory	Standing bath (150-160°F., 20 min.). Hot air dryer (200°F.), 1 lb. wool to 2.4 gal. liquor. (20% Aridex WP on weight of wool)
32 oz. outer clothing fabric	1	Batch	Laboratory	Standing bath (140-150°F., 20 min.). Hot air dryer (200°F.). Hoffman Press. 1 lb. wool to 2.4 gal. liquor (20% Aridex WP on weight of wool).

TABLE IV

Relative Exhausts of Aridex WP at 120° F. Under Controlled Conditions

Fabric	*Percentage Exhaust* 0.1% *Emulsions*	1.0% *Emulsions*
Viscose Rayon		
Crepe (boiled off)	40	<20
*Crepe (boiled off)	60	<20
Cotton		
80/80 bleached, unfinished muslin	50	<20
*80/80 bleached, unfinished muslin	70	<20
Wool		
Broadcloth (scoured)	60	<20
*Broadcloth (scoured)	>80	<20
Natural Silk		
Crepe (boiled off)	80	<20
*Crepe (boiled off)	100	<20

* These fabrics were rendered very slightly alkaline before use. The alkaline condition of the fabrics was not, however, great enough to "break" the emulsions.

ratory and practical scale applications. The information covering the commercial applications is in some cases fragmentary, of necessity. The data should be of value as a guide in determining the best concentration of Aridex WP and the best procedure for any particular case.

Water-repellency was tested by several methods, depending on the construction of the fabric and on the requirements. No single test was used as a standard, but the three tests used most frequently were (1) the hydrostatic pressure test suggested by the A. A. T. C. C. (1934 Year Book, page 156), (2) a water-absorbency test, and (3) a spotting test.

APPLICANTS FOR MEMBERSHIP

Associate

William Atkinson—Sales Engineer, National Vulcanized Fibre Co., Wilmington, Del.

J. Clinton Bach—Salesman, Bick & Co., Inc., Reading, Pa.

Jacob Pfister—Manager, Calco Chemical Co., Providence, R. I.

John B. Williams—Secretary and Salesman, Charles H. Stone, Inc., Charlotte, N. C.

Student

Elmer F. Brano—Philadelphia Textile School. Sponsor: E. C. Bertolet.

Alda J. Cherr—Lowell Textile Institute. Sponsor: L. A. Olney.

Crock Testing and Recording Machine

Crocking or rubbing tests have long been the cause of disputes. Some people crock hard, some people easy. The dyer or seller cannot tell if the same cloth will please the agent, selling house, or purchaser today or tomorrow. The chemist cannot tell if his process is a little worse or a little better, because the test is uncertain and he can't be sure.

The Research Committee has had for some years a Sub-Committee on Crocking of which Dr. Hans Meyer is chairman. The matter seemed more and more important until finally machines for definite results began to be made. One of these seemed cheap enough for general use and was quickly taken up at the suggestion of Professor Olney. This machine was designed by Mr. Walter C. Durfee. It makes crock records on 2" by 2" squares of cotton, which are held by a ring on the crocking finger of the machine.

These are very definite, and widely admitted to be definite, and very useful. The records are clipped to the goods; or otherwise kept. It makes a definite referee between the dyer, agent, seller, buyer, etc.

The first design was made hastily for use in the laboratory of the W. C. Durfee Co., Inc., and rapidly improved by consulting with various textile people.

This machine, which has been accepted as the standard for the American Association of Textile Chemists and Colorists by the Research Committee, has a round finger of diameter five-eighths of an inch, length of stroke four inches, and a force on the crocking finger of two pounds. Unsized white cotton cloth is specified for the tests. (The Committee tentatively suggests 20 double strokes as the most useful for comparison tests between dyer, chemist, agent, and buyer.)

These crock recording machines, "Crock Meters," may be purchased directly from the Association, care of Lowell Textile Institute, Lowell, Mass., or from the makers, W. C. Durfee Co., Inc., 114 Federal Street, Boston, Mass. The price is $10 postpaid.

UNEMPLOYMENT REGISTER

Members of this association, who are without employment, should forward to the secretary a statement as to their qualifications and experience. This information will subsequently appear on these pages with an identifying key number. Employers are also requested to file with the secretary any vacancies which may occur in their businesses.—H. C. Chapin, Secretary, Lowell Textile Institute, Lowell, Mass.

Key: A—Laboratory and research; B—Dyeing or printing; C—Finishing; D—Sales; E—Instruction; F—Executive.

NOTE: PERSONS WHO HAVE OBTAINED EMPLOYMENT SHOULD NOTIFY THE SECRETARY OR THE AMERICAN DYESTUFF REPORTER AT ONCE. Prospective employers may file vacancies either with the secretary or the American Dyestuff Reporter.

A-6

Education—Analytical Chemistry and Dyeing Course, Lowell Textile Evening School.

Experience—Seven years as print color and dye chemist in printing, dyeing and finishing plants; recently in charge of textile printing department of dyestuff manufacturer.

A-B-2

Education—Lowell Evening Textile School, 1917.

Experience—Five years' experience in hosiery dyeing, full fashioned hosiery of silk and cotton and silk, also men's hosiery containing rayon, wool, cotton and celanese. Several years experience in laboratory work. Has also had experience in jig-dyeing of cotton piece goods, slub and top dyeing.

A-B-4

Education—B.T.C. 1934, Lowell Textile Institute.

Experience—Assistant chemist in cotton knitting plant; second-hand in woolen knit goods dye house. Will go anywhere; references.

A-B-5

Education—Graduate of the University of Lausanne, Switzerland. Doctor's degree in Chemistry. Knowledge of French and German.

Experience—Eleven years with large bleaching, dyeing, printing and finishing plant as assistant Chemist and then Chemist in charge of the Laboratory. Experience in dyeing and printing cotton and rayon fabrics; research and analytical work. Woman.

A-B-7

Education—Evening school in textile dyeing.

Experience—2 years laboratory in dyehouse; 9 years dyer and foreman on hosiery, ribbons and rayon; 2 years assistant to superintendent. Can handle help efficiently. Desires position as supervisor or demonstrator of dyestuffs. Age 30; married. Prefers vicinity of New York.

A-B-C-2

Education—Graduate of Lewis Institute of Engineering of Chicago and graduate of Philadelphia Textile School (Chemistry and Dyeing department).

Experience—Has had extensive experience as assistant chemist and colorist in silk printing, dyeing and finishing; also dyeing raw stock wool; and dyeing and finishing cotton and rayon. Age 30; married; references.

A-B-C-3

Education—3 years at Brown University and Drexel Institute.

Experience—2½ years in dyestuff laboratory; 3 years as second-hand, dyeing indanthrene and direct colors on rayon skeins; 6 months as boss dyer on silk and cotton ribbons and hosiery; 3 years overseer of dyeing and finishing rayon tubing. Can handle laboratory, dyehouse, finishing or outside service. Age 30; married.

A-B-C-F-1

Education — Five years chemistry and engineering, Brown University (Evenings).

Experience—1 year general superintendent at print works (shirtings, dress goods, etc.; cotton and rayon). 12 years chief chemist and superintendent of large bleachery and dyeworks (cotton, rayon and silk piece goods). 4 years chemist in charge of control work in bleach, print and dye works (cotton, wool and rayon piece goods). 9 years chief chemist and assistant superintendent in gas and oil manufacture. Practical dyer and finisher and can handle help efficiently and get results. Can help a plant seeking to improve their vat dyeing, shrinkage results, finishes and service to customers. Age 45; married.

A-C-1

Education—4 years at Newark Evening Technical School in Chemical Engineering.

Experience—8 years in manufacturing, research, testing of soaps, oils, gums and finishes and application of same in all phases of the textile industry. Age 23, single. References.

A-E-1

Education—Ph.D., Univ. of Illinois, studied chemical engineering at Columbia, licensed chemical engineer, New Jersey.

Experience—10 years' experience teaching in colleges, subjects included chemical and textile subjects. Has had broad experience in industrial work including experience in testing materials, research and consulting. Will go anywhere; references.

B-1

Education—Educated and trained in chemistry and calico printing in Glasgow, Scotland.

Experience—Has been with large print works as colorist for 13 years producing first class work on cotton, rayon, wool and silk fabrics. References.

B-2

Experience—Boss dyer with one firm for 18 years, divisional supt. at print works for 1 year, in charge of processing and dyeing of cottons and rayons at large bleachery for 6 years. Prefers bleachery in East but will go anywhere. References.

B-3

Experience—Foreman piece dyer for the past 21 years. Can dye the following: celanese, rayon, cotton backs, wool, silk and mixed fabrics. Has knowledge of finishing and laboratory work.

B-6

Education—Graduate R. I. School of Design.

Experience—5 years in bleachery, 7½ years as assistant dyer, 2 years as boss dyer and 3 years as superintendent of dyeing and finishing. Married, 33 years old. References.

B-7

Experience—Eight years as boss dyer on skeins and ribbons. Over ten years as chemist and head dyer for a large hosiery mill. Experienced on Silk, cotton, rayon and wool in skeins, ribbons, piece goods and all kinds of mixtures. Willing to go anywhere. Not afraid to work or face responsibility. Can handle help efficiently.

B-8

Education—Chemistry and Dyeing Department, Philadelphia Textile School.

Experience—Eleven years experience as chemist and boss dyer on the following: woolen, worsted and cotton yarn; woolen, worsted and union piece dyes on both ladies' and men's wear; wool, cotton, shoddy and mohair raw stock. Age 33, married, will go anywhere. References.

B-9

Experience—Hosiery dyer with fifteen years' experience on high grade silk hosiery; familiar with all types of machines. Age 43, married. Will go anywhere.

B-14

Education—Rhode Island School of Design.

Experience—Familiar with all classes of wool dyeing. Seven years with large carpet mill as dyer and processor of washed oriental rugs. Will go anywhere, married, 37 years old. References.

B-15

Education—B.T.C., Lowell Textile Institute, 1934.

Experience—Experience in dye house running washers, dye kettles and as a dye weighter.

B-17

Education—Lowell Textile Institute (Chemistry and Dyeing Course) 1916; extension courses at Brown University.

Experience—6 months dyeing wool at finishing company; 2½ years research work on bleaching, dyeing and finishing at dye works; inspector of textile equipment, U. S. Ordnance Dept., during war; 15 years as superintendent of dyeing at finishing company, including all types of colors on cotton piece goods and some rayon and celanese; handled chemical work at last named plant for many years as well as dyeing. Age 40, married, prefers East. References.

CALENDAR OF COMING EVENTS

Outing, Rhode Island Section, June 19, 1936.

* * *

Annual Outing, Philadelphia Section, June 19, 1936, Whitemarsh Valley Country Club, Whitemarsh, Pa.

* * *

Outing, Mid-West Section, Ridgeway Country Club, Oshkosh, Wis., June 20, 1936. Luncheon at noon in the Club House; dinner in the evening at Hotel Rauf.

* * *

Outing, New York Section, North Jersey Country Club, Paterson, N. J., June 26, 1936.

* * *

Summer Meeting and Outing, Piedmont Section, June 27, 1936, Ocean Forest Hotel, Myrtle Beach, S. C.; reservations through Mason Alexander, manager.

* * *

Annual Meeting, Providence, R. I., December 4 and 5, 1936.

AMERICAN
DYESTUFF
REPORTER

LOUIS A. OLNEY, Sc.D.
Professor of Chemistry and Dyeing, Lowell Textile Institute
Directing Editor

A. P. HOWES, Publisher

NORMAN A. JOHNSON
Managing Editor

MYRON DREW REESER
Advertising Manager

Published biweekly by
HOWES PUBLISHING CO., INC.
440 Fourth Avenue, New York City

Subscription price: $5.00 per year; Canadian $6.80; foreign $6.00

Vol. 25 June 15, 1936 No. 12

JAPANESE DYESTUFFS

IN view of the considerable interest and controversy which has lately arisen concerning textile materials, particularly cotton fabrics, which have been produced in Japan and sold in this country, special interest is to be found in figures which have been recently released by the Bureau of Foreign and Domestic Commerce of the Department of Commerce regarding Japanese production of artificial dyestuffs, intermediates and other coal tar products. The latest figures quoted are for 1934, but by comparison with the immediately preceding year they give an indication of the trend of this industry in Japan.

According to the report there were, at the end of 1934, 54 factories manufacturing dyestuffs and intermediates, 8 producing intermediates only, 16 manufacturing medicinal chemicals, 4 producing perfumes and 2 other coal tar products. The industry employed 1,251 of what are referred to as "engineers" and 7,760 other workers. The aggregate value of production for that year amounted to 36,472,008 yen.

The report further states that the production of dyestuffs in 1934 totalled 17,117,723 kilos, an increase of 1,142,884 kilos, or 7 per cent, over the preceding year. The rapid rate of increase for the past few years is clearly shown in the table below.

The total value of the dyestuff production for 1934 amounted to 22,497,669 yen divided among the various classes of colors in the following proportions: basic—17.92 per cent; direct cotton—27.46 per cent; acid—7.67 per cent; acid mordant—3.38 per cent; mordant—1.19 per cent; sulfur—24.15 per cent; vat—14.56 per cent; and other colors 3.67 per cent.

Of fifty important manufacturers of dyestuffs and intermediates, twenty-five are manufacturing dyestuffs only, seventeen are manufacturing dyestuffs and intermediates and eight are manufacturing intermediates only. Of the twenty-five dyestuff factories, one was started in 1915, five in 1916, three in 1917, one each in 1918, 1920, 1921, and 1923, three in 1929, one each in 1931 and 1932, *six* in 1933 and one in 1934. Of the seventeen dyestuff and intermediate factories, three were started in 1916 and two in 1918 and one in each of the following years: 1902, 1908, 1914, 1915, 1917, 1919, 1920, 1922, 1926, 1931, 1932 and 1933. Of the intermediate factories one was started in 1906, one in 1917, two in 1928, one in 1916, two in 1932 and one in 1934.

The rapid growth of the dyestuff industry in Japan is easily seen from a study of the production figures given in the table below. While no official reports have been made for production during 1935 it is to be assumed from the data which is available that the dyestuff production was extremely active in view of the fact that all branches of the Japanese textile industry established new records for production and exports which would naturally increase the demand for dyestuffs. Inasmuch as dyestuff exports during 1935 totaled 19,583,000 pounds and the imports were only 2,771,000 pounds the domestic production must have been considerably higher than consumption.

Increased production was not confined to dyestuffs and intermediates as is shown by the following reports of the Japanese Department of Commerce and Industry regarding the output of leading concerns for some of the more important industrial chemicals: caustic soda—1934: 165,428 (all figures are metric tons); 1935: 213,319; soda ash—1934: 165,292; 1935: 198,304; sulfur—1934: 116,244; 1935: 138,271 (January to November); bleaching powder—1934: 64,981; 1935: 74,254; aniline:—1934: 3,391; 1935: 3,660.

While as yet the Japanese chemical industry has not attained world-wide prominence, there is indication that if the rapid expansion of the past several years continues it will have considerable effect upon the chemical markets of the world. With the cheap production costs prevailing in that country, a possible menace to our chemical industry is developing.

Production of Dyestuffs, 1930-1934 Inclusive

Unit—kilo

	1930	1931	1932	1933	1934
Basic colors	257,633	316,782	566,453	725,743	814,835
Direct colors	609,363	744,321	1,321,467	1,748,151	2,011,985
Acid colors	239,627	217,444	393,550	459,236	498,030
Acid mord colors	41,568	31,555	140,056	240,082	198,665
Mordant colors	20,783	27,631	14,622	11,895	40,088
Sulfur colors	6,472,947	8,106,895	11,172,731	12,008,372	12,522,459
Vat colors	94,452	139,614	240,109	657,910	784,018
Other colors	43,993	75,138	194,113	121,450	245,643
TOTAL	7,780,366	9,659,380	14,043,101	15,972,839	17,115,723

Washington News Letter

By WALDON FAWCETT

UNLESS all signs fail, the period just ahead should prove one of the most favorable seasons in a long interval for Governmental research in all technical fields. To begin with, it is proverbial that, other things being equal, a Presidential campaign year is a time advantageous for Federal undertakings in scientific research. The explanation is that most projects in this category are non-controversial in character. Or, at least, are lacking in the elements that incite political debate. Incidentally, executives in the Departments have more time to devote to research programs inasmuch as, in election year, there is restraint in the initiation of the type of general administrative policies that engender opposition or serious criticism. Assumption that election year is auspicious for explorative or routine research is contingent, of course, upon the availability of ample allowances in the budget. Fortunately, the 1936-37 purse will answer. Indeed, the appropriations for research are the most generous since the beginning of the business depression.

NEW EQUIPMENT NEEDED FOR STANDARDS BUREAU

Apropos of current appropriations, it may be worthy of mention that this is the first year that the Government's foremost research institution has operated under a new system of appropriations whereby the number of appropriation items is reduced from 29 to 4. Director Lyman J. Briggs declares that the new consolidated system at the National Bureau of Standards is operating very satisfactorily and that a simple system of cost accounting has been perfected which enables the officials to check closely the amounts which are called for and expended under the main appropriation items.

In asking, for next year, a considerable increase in appropriation, the heads of the Standards Bureau sought authorization for replacement of equipment which they feel cannot longer be postponed. Much of the equipment at the Bureau is 25 to 30 years old and has suffered from deterioration to the point where efficiency is affected, or inadequacy results. This is the situation, for example, with the electrical transformers. The present installation is not large enough to carry the full load which is imposed upon them at times. When this happens the entire plant shuts down and work stops throughout the Bureau. Some new equipment is needed in order to keep step with changes of practice in manufacturing industries. For example in the case of tire fabrics. Mainly, though, the heavier demands upon the budget are due to the increase in the volume of testing work, the tests this past year having exceeded by 15 per cent the volume in the preceeding year.

RESEARCH WORK CIRCUMSCRIBED

Readers of the REPORTER will regret that there is no assurance of resumption of operation of the experimental cotton mill at the National Bureau which shut down two years ago for lack of funds. The Bureau will not receive in 1937, for Research and Development, funds much if any in excess of the two-thirds of a million dollars which Congress voted for 1936. A victim of the policy of continued economy is the only experimental cotton mill in the country available for research work. When legislation was under way at the present session, Congressmen were fully informed of the value to textile mill technologists and textile schools of the interrupted program of study of the relationship between properties and construction of various fabrics in order to demonstrate the textile construction best adapted for a particular purpose.

A notable project in the list of extensions of research activity is the comparative investigation of methods of dry cleaning fur garments with the purpose of ascertaining the process least liable to work injury to furs by removal of oil from the skin. The fur interests as well as the National Association of Dyers and Cleaners have requested determination of this controversial issue and it is understood will defray a portion of the expense. Compelled to pick and choose new research undertakings from many candidates the decision to proceed with the fur inquiry was influenced in part by the circumstance that the Government has a direct interest in the fur processing owing to Federal supervision of the Alaska seal herds. Just here, by the by, is revealed a principle of administrative policy at the Bureau of Standards that is, perhaps, not clearly understood in technical circles. In making selections of new ventures in research, officials at the Standards Bureau take the position that they must limit investigations to those which are of immediate interest both to the Government and to some broad industrial or consumer group. The fur project, above mentioned, is an example of research sought with equal insistence by both the commercial—technical and consumer groups.

In a recent expression, Dr. Briggs cited another immediate need as follows: "Oxidizing agents attack cellulose in the presence of water to produce materials which are known as oxycellulose. This change profoundly modifies the properties of the original material, but what the final products are, or what factors influence the rate of reaction is unknown. This matter is of great practical importance in the bleaching of cotton goods and also in their protection in service, and should be thoroughly studied."

The Director, at the same time, made mention of the need for further expansion in the Optics division of the Bureau program, a section which is already known for its operations in the development and maintenance of color standards, etc. He commented as follows: "New lines of work which the Bureau should undertake include the development of methods for measuring the turbidity of solutions which has a wide application in scientific and chemical engineering fields, and the development of wavelength standards in the extreme ultra-violet region of the spectrum".

With all the other demands upon it, the Bureau of Standards continues to give a share of its attention at all times to research in behalf of the development of standard methods of chemical analysis. The theory is that this is an obligation inasmuch as the Bureau is called upon to make chemical analyses of the highest attainable precision and these analyses will carry confidence in their accuracy only if the analytical methods used are unimpeachable.

CHANGING ATTITUDE ON DESIGN PROTECTION

One of the most interesting developments of the later reaches of the 74th Congress has been the changes on the part of the forces of general business in sentiment with respect to protection of original designs. By way of preface to the current news, it should be remarked that there has been a realignment but no extensive modification of the cleavage which has long existed on the basic issue of improvement in the facilities for safeguarding unique or distinctive patterns. Within the past year or two, additional industries, suddenly become more conscious of their design—dependence, have moved to make common cause with the textile industries in the quest for less expensive and more elastic Federal certification of designs. But a number of industries, which are seemingly predicated upon assets of style or design, continue unabated their resistance to any reformation of design arrangements which would embrace their lines.

The reversal of position lately manifested is wholly in respect to the proposition for limited or piece-meal Design Copyright. As our readers know, the conservers of textile designs were moved to propose a plan for registration of textile designs only when it became apparent that the original plan for general Design Copyright was to encounter irreconcilable opposition. Up to now, though, this alternative devised by the textile forces, has been obliged to face three obstacles. First, an attitude of active opposition on the part of certain industrial groups that want no design monopolies in their own zones and are apprehensive that a textile concession might be the opening wedge for a progressive movement. Second, an attitude of indifference but implied criticism on the part of the other antis who regard the textile experiment as none of their affair. Third, the chronic resistance in Congress to legislation that is accounted very special by reason of its narrow application.

That there is a new undertone throughout the prejudiced and the neutral industrial groups is due to the passage by the Senate of the Duffy Copyright Bill attached to which is the Vandenberg Amendment for Design Copyright. When this Bill arrived in the House of Representatives the dissenters discovered that they were face to face with a real threat of universal Design Copyright. Their reaction has been to change from a passive to an active attitude and to advocate enactment of the Sirovich Textile Bill (H.R. 5859) in lieu of the Duffy Bill. In other words, the industries that desire to be let alone, with such consolation as the Design Patent system accords, have been converted to advocacy of industry-by-industry protection for design. As the lesser of two evils, they are now ready to accept zoned Design Copyright, hoping that it is only for the other fellow. To appease the textile group and other industries asking relief the erstwhile silent opposition has voiced support at the hearings before the House Committee on Patents. Incidentally, there has not been lost upon the converts to compromise the inevitable effect in the textile field and elsewhere of the action by the Federal Trade Commission against the Fashion Originators Guild, the National Federation of Textiles, etc.

THE INCREASE IN DESIGN PATENTING

Meanwhile, behold a continuance of that spurt in design patenting which is something of a mystification to onlookers. An increase within a year of more than 25 per cent in the number of applications for patents on design appears to require explanation beyond the creation, in the Patent Office of a Division devoted to Designs and an attendant quicking of the clearance of designs which are seasonal in character and consequently in need of expedition in examination. The fact that the increase in the volume of design patents, from 3,800 to nearly 5,100 in the last fiscal year, was coincident with a decrease in the number of trade mark applications has suggested to some observers that industry may be turning from brands to designs as mediums of commodity identification. Officials at the Patent Office scout this theory and attribute the trade mark recession solely to a cessation of certain activities surrounding prohibition repeal. The guess at the Patent Office is that the gain in design patenting has been contributed by interests which have decided that their protective policies cannot wait upon the institution of Design Copyright.

AMENDMENT OF THE CLAYTON ACT

For textile chemical interests there are contracts more numerous and of wider scope than has been generally sensed in the program for extension of the Clayton Act which has emerged as a major legislative objective in the second session of this Congress. On its face, this substitute for the independent Fair Trade Act which was first proposed, is essentially a measure for regulation of pricing methods. In reality the underlying purpose is to

supply a lack, discernible with the passage of time, in both the Sherman Act and the Clayton Act. Providing, by the supplement, a broadly applicable and elastic addition to the anti-trust laws designed to insure, in so far as practicable, equality of opportunity in business.

Inspired, admittedly, by disclosures in the recent Chain Store Investigation, the Bill sponsored by the Committee of the Judiciary has struck at any discrimination in price or terms of sale between purchasers of commodities of like grade and quality. Not merely direct concessions in prices but all manner of separate allowances to favored customers. For example, a ban on brokerage allowances except for services actually rendered. Such, indeed, are the terms of indictment as to necessitate henceforth a close scrutiny of all forms of "service" in connection with sales.

Of possible interest to technical personnel is the more precise definition that may of necessity be applied to business "overhead" in consequence of this legislative trend. In encouragement of improvement and economies in process of manufacture, methods of sale, and modes of delivery legality is granted to bona-fide cost differentials actually arising in operation or overhead. But only differentials traceable to specific items or lines are allowable, rather than pro rata credits against savings in overhead on volume of business as a whole. "Service allowances" for all manner of sales promotional purposes are under challenge by the new code—albeit payment is allowed for space at trade associations exhibitions. "Loss leaders" are pointedly under indictment and there is prohibition on "brokerage" allowances except for services actually rendered. The basing point method of sale would be rendered indefensible by the new strictures.

—♦♦—

The Nature of Cellulose

(Continued from page 318)

the form of their micellae or even of aggregates of micellae as was pointed out by *McBain* (1926)[41]. *Staudinger,* [42], however, put forward the hypothesis that the high concentration in which nitric and sulfuric acid are applied for the process of nitration may prevent these acids from undergoing dissociation and thus prevent degradation of the cellulose. He therefore assumes that in nitrocellulose solutions one deals with the very long chain molecules and that their length comes closest to that of native cellulose as it exists in the plant.

As regards the phenomenon of *coagulation,* an ever-interesting example in the cellulose field is offered by the viscose process, of which *Wolfgang Ostwald* in his book on "Theoretical and Applied Colloid Chemistry" (1917) remarked that "it is naturally honey-combed with colloidal-chemical phenomena," and that "the process of coagulation of viscose probably represents the best studied of the whole line of coagulations in emulsion colloids"[43].

Although during the years since 1926 an enormous quantity of experimental data has accumulated, the fundamental principles of the process as they were put forward by the inventors, *Cross* and *Bevan* (1893)[44] and were supported by the investigations of *Ost* and *Westhoff* (1911)[45] and later on broadened by *Schuster* and myself (1926)[46], as well as by *Berl* and *Bitter* (1926)[47], appear still unshaken. No doubt it would pay to review the experimental data published since 1926 and to try to join them into the picture which those earlier investigations have drawn whereby the development in X-ray investigation and colloid chemistry would aid to modern interpretation. However, today the time available forces us to postpone this undertaking to another opportunity.

In concluding, I hope that I have been able to show the enormous progress which cellulose chemistry and physics have made since the starting year of this review, progress which also has opened manifold new fields for investigation of problems calling for penetration into their elusive but most attractive secrets.

Bibliography of Part IV

[1] A. Quincke Ann. Chim. Phys. *113,* 513 (1861).
[2] Mills and Talkamie J. Chem. Soc. London *9,* 153 (1883).
[3] Mueller- Jacobs J. Soc. Dyers & Col. *11,* 95 (1855).
[4] Cross and Bevan, Researches II, p. 116 et seq.
[5] O. N. Witt, Chem. Techn. d. Gespinstfasern 1888, p. 369.
[6] Cross and Bevan loc. cit. p. 7 and 177.
[7] C. G. Schwalbe, Die Chemie d. Cellulose, Gebr. Borntraeger, Berlin, 1911, p. 356 et seq.
[8] Wolfgang Ostwald, Theoret. and Appl. Coll. Chem. (transl. by M. H. Fisher), Wiley and Sons, New York, 1917, p. 208 et seq.
[9] E. Heuser, Prefaces to Textbook of Cellulose Chemistry and to Lehrb. d. Cellulosechemie, 3rd ed.
[10] H. Mark, loc. cit. Chapter II, note No. 35.
[11] M. J. Duclaux, Rapp. sur les Hydrates de Carbone (10th conference, union intern. de Chimie, Liège, 1930) p. 214 et seq.
[12] Clayton Beadle, Chapters on Papermaking, Vol. 1 and Vol. 5.
[13] J. Strachan, Proc. Techn. Section Paper Makers' Assn. Gt. Britain and Ireland, Vol. 2, Pt. 2, London 1926. World's Paper Trade Rev. Nov. 20th, 1925.
[14] Complete compilation of literature on the subject in J. H. Bell, The Effects of Beating, Thesis, Un. Edinburgh, also issued by Techn. Section Paper Makers' Assn., London, 1934.
[15] W. B. Campbell, Can. Forest Service Bulletin No. 84, Ottawa 1933; Pulp & Paper of Canada, *36,* 178 (1935).
[16] H. Mark loc. cit. Chapter II, note No. 46.
[17] G. Champetier, loc. cit. Chapter I, note No. 45.
[18] J. A. Katz, Transactions of the Faraday Soc. *29,* 279 (1933); Kolloidchem. Beihefte *9,* 1 (1917).
[19] H. Mark, Physik und Chemie der Cellulose, p. 95 et seq.
[20] J. A. Katz, Transact. Faraday Soc. loc. cit.
[21] See also H. Hulshof, Amsterdam Kon. Akad, *33,* 166 (1930).
[22] R. L. Steinberger, Textile Research (U. S. Inst. for T. R.) *4,* 451 and 531 (1934).
[23] W. B. Campbell, Pulp & Paper Can. loc. cit.
[24] E. Heuser, Zeitschr. Angew Chn. *37.* 1010 (1924); with W. Niethammer, Cellulosechemie *6,* 14 (1925); with Bartunek Cellulosechemie *6,* 19 (1925); with Bartunek and Schuster, Cellulosechemie *7,* 29 (1926).
[25] Heuser and Bartunek, Cellulosechemie *8,* 31 (1927).
[26] W. D. Bancroft and J. B. Calkin, loc. cit. Chapter II, note No. 34.
[27] G. Champetier, loc. cit. Chapter I, note No. 45.

[29] K. Hess and O. Schwartzkopf, Zeitschr. Phys. Ch. (A) *163*, 395 (1933).
[30] K. Hess and C. Trogus, Zeitschr. Phys. Ch. (B) *11*, 381 (1931).
[31] S. M. Neale, J. Soc. Chem. Ind. London, *50*, 177 T (1931).
[32] E. Heuser and M. Schuster, Cellulosechemie *7*, 17-55 (1926).
[33] Traube, Ber. d. D. Ch. Ges. *54*, 3220 (1921); *55*, 1899 (1922); *56*, 268 (1923).
[34] K. Hess, Die Chemie der Cellulose, 189 et seq.
[35] H. Mark, Physik und Chemie der Cellulose, 232 et seq.
[36] See e. g. Wolfgang Ostwald, Grundriss der Coll. Chemie (3rd ed.), Dresden, 1912.
[37] E. Berl and Klaye, Zeitschr. f. Schiess-und Sprengwesen *2*, 381 (1907); *4*, 81 (1909); Berl and Buetler, loc. cit. *5*, 82 (1910).
[38] H. Ost, Z. Agnew. Ch. *24*, 1892 (1911).
[39] W. H. Gibson, J. Chem. Soc. London, *117*, 479 (1920).
[40] H. Staudinger, Die Hochmolek. Org. Verb., see Chapter I, note No. 37.
[41] H. Staudinger, Naturwissenschaften *22*, 53 (1934); see also E. Heuser and Bartunek in E. Heuser, Lehrb. Cell. Chemie 1927; p. 176 (decrease of viscosity of cotton cellulose in solution and increase of solubility of the regenerates in alkalies with time on standing in solution).
[42] B. J. McBain, J. Phys. Chemistry *30*, 245 (1925).
[43] H. Staudinger, Naturwissenschaften, loc. cit. 802 (1934); Cellulosechemie *15*, *66* (1934).
[44] Wolfgang Ostwald, loc. cit., see note No. 8, p. 208 and 209.
[45] Cross and Bevan, Cellulose, 2nd ed. Longmans, Green and Co., London, 1903; Cross, Bevan and Beadle, Ber. D. Ch. Ges. *26*, 1090 (1893).
[46] Ost, Westhoff and Gessner, Ann. d. Ch. *382*, 340 (1911).
[47] E. Heuser and M. Schuster, loc. cit., see note No. 31.
[48] E. Berl and Bitter, Cellulosechemie *7*, 137 (1926).

CONCLUSION

New Products—Trade Notes

• FULTON RELEASES

Fulton Dye & Import Co. announces release of the following new products:

Acid Light Yellow 5 J A—a new patented acid dyestuff brought out by Societe Anonyme des Matieres Colorantes et Produits Chimiques de Saint Denis. It is recommended by the distributors for dyeing wool in a sulfuric acid bath and yields an exceptionally green, bright yellow which, it is stated, has an extreme light fastness which, it is claimed, was heretofore not possible in the very green shades of yellow. It is said to be suitable either alone or mixed with other acid dyestuffs fast to light and presents the possibility of obtaining many fast-to-light shades that have heretofore not been available. It is claimed that this color does not stain fabrics of cotton, viscose or acetate and that unions of wool and silk are uniformly dyed.

Direct Light Blue B V A—a new patented dyestuff said to be different from all other products actually on the market. It may be used for dyeing vegetable fibers as well as weighted and unweighted silk. It is said to be dischargeable to a clear white. It is further claimed that it is not sensitive to hard water, metallic salts or organic acids. It is also stated that it leaves cellulose acetate effects unstained and because of its very bright green shades is said to lend itself to combining with yellow to produce greens. It is stated that it levels well and that its light fastness is excellent.

Acetoquinone Blue N N R Powder—an acetate color brought out by Compagnie Nationale de Matieres Colorantes et Manufactures de Produits Chimiques du Nord Reunies Etablissements Kuhlmann. It is especially recommended by the distributors for its exceptional drawing properties in dark shades, not only on the lustered but on the pique mat albene acetate. It is said to be very suitable for the production of the two-tone shade effects on mixed materials as the vegetable fibers are well reserved and animal fibers slightly stained. A generally good fastness is exhibited.

• BATTLE OF PURITY

The Atlantic Refining Co. has published a booklet entitled "Battle of Purity" which describes their white oils. Copies of this booklet as well as experimental samples are available upon request.

• 37th ANNUAL REUNION, L.T.I.

The 37th Annual Reunion of the Lowell Textile Institute Alumni Association was held in Lowell, Mass. on Saturday, June 6th at the Institute. A special feature of the reunion was an exhibition of new apparatus, machinery and processes which were demonstrated and explained by members of the instructing staff. A meeting of the newly formed alumni athletic association was held at 11 A.M. This was followed by lunch and a business meeting. The class of 1936 then dedicated a new campus gate. Baseball and golf occupied the attention of the visitors during the afternoon and the banquet at Vesper Country Club in the evening concluded the festivities.

• OUTING, S. O. M. A.

More than fifty members of the Sulfonated Oil Manufacturers Association and their friends gathered at Buckwood Inn, Shawnee-on-the-Delaware, Pa., on June 3rd and 4th. The usual formal business meeting was not included in the program, thereby giving those in attendance an opportunity to enjoy to the full the beautiful Shawnee Country Club golf course in addition to a variety of lighter indoor sports.

This group had its first meeting of this type at the Manufacturers' Country Club at Philadelphia last September, and the results were so satisfactory that the Social Committee of the Association was requested to arrange for a second meeting of this character for which Shawnee was selected. The Committee responsible for the success of the field day consisted of Fred C. Scholler, Chairman, C. P. Gulick, H. B. Hooper and John C. Wolke.

Golf on the 4th was followed by vocal and instrumental entertainment, and particularly by a series of feats of magic and sleight of hand which held the entire group until late in the evening.

The golf prizes were awarded at the end of the closing dinner, June 4th, as follows: Low net for members, Robert W. Brewer, of Liberty By-Products Co., Butler, N. J. Mr. Brewer had a gross score of 79, a club handicap of 6, and played the last nine holes in 33; low net for guests, F. R. Lavezzo; second low net member, R. A. Scher; low gross member, Lloyd Koons; kickers handicap for members, B. A. Schiller; low gross guest, K. L. Patterson; third low net, E. E. Yake; fourth low net, E. S. Atkinson; highest gross score member, H. B. Dohner; highest gross score guest, A. P. Gumaer; door prize guest, A. A. Underwood; door prize member, H. B. Hooper; fifth low net, H. B. Sweatt, sixth low net, J. C. Wolke; highest net score, member, Sam Slavin; birdie on 16th, D. S. Whiteman.

The S. O. M. A. silver cup won last September by Robert A. Scher was awarded to Robert W. Brewer for low net.

• SANDOZ RELEASE

Sandoz Chemical Works announces release of the following new shade card:

Wash Fast Colors on Pure Silk—which illustrates a range of Sandoz' best wash fast colors for pure silk. This card should be of interest for the dyeing of such fabrics as dress, underwear, glove and ribbon materials where a high degree of fastness to washing is required. As the methods of dyeing the colors vary somewhat three methods are given and the method to be used for each color is indicated. Shade Card U. S. 23.

• ACQUIRES NEW DYEING PLANT

The Western Dyeing and Processing Company is to become a subsidiary of the Franklin Process Company in Providence, R. I. The new company will be known as the Western Franklin Process Company and will occupy the plant that is now used by the former company in Chicago.

William Stahl will be president and general manager of the new company and, with the support and assistance of the parent company, will be able to improve and extend the facilities that he has already been offering to the trade.

The latest type of Franklin Process package dyeing equipment will be installed and also the very latest type of winding and other accessory machinery.

The contemplated changes will be made without any interruption in production.

• PHILADELPHIA BRANCH, A.A.P.

Effective today, the new address of the Philadelphia Branch of American Aniline Products, Inc., will be 210 North 13th Street. The space was remodeled to accommodate a full suite of offices, a new, completely equipped laboratory and modern warehouse facilities. Complete stocks will be maintained to assure rapid delivery service in Philadelphia and vicinity.

• RAYON ANNIVERSARY

The 25th year of American Rayon Production will probably be celebrated by a National Rayon Technical Conference this November. The Textile Division of the American Society of Mechanical Engineers has extended an invitation to the American Association of Textile Chemists and Colorists, Committee D13 of the American Society of Testing Materials and the U. S. Institute of Textile Research to join with the Division in being co-sponsors of a National Rayon Technical Conference to be held in Baltimore in November of this year.

C. H. Ramsey, Chairman of the A. S. M. E. Textile Division extended the invitation to the other Societies and asked them to send representatives to a program committee meeting to be held in New York City, June 15th. Mr. Ramsey suggested a two day conference and pointed out the wonderful opportunity this anniversary conference would give to the technical men of the industry to meet together to exchange experiences. The suggestion that Baltimore be the city was for a two fold reason, first because rayon started production there 25 years ago and second, it was centrally located between the northern and southern sections of the industry. Mr. Ramsey stated that initial expenses of getting the conference under way had been underwritten by the A. S. M. E. but that the Conference was expected to be self-supporting by charging a small registration fee.

• NEW CLEANER

A dry-cleaning fluid has been recently developed by E. H. Bronson, consulting solvents chemist, in the laboratories of the Solvex Products Company, New York City.

This new cleaner is known as Solvex No. 7 and has been especially formulated to cope with the cleaning problems peculiar to the piece dyeing and finishing industry. A product of exhaustive research, Solvex No. 7 is said to presuppose and fulfill three major requisites:—first, it is said to remove stubborn grease and oil spots as well as other troublesome stains from silks, rayons, acetates, cottons, and mixtures,—easily and completely; second, it is stated that the cleaning action, highly effective as it is, in no wise can injure the texture, fiber or color of the fabric; and third, it is claimed to be singularly free from explosive vapors.

• GENERAL RELEASES

General Dyestuff Corp. announces release of the following shade cards and circulars:—

Naphtol A S on Mixed Fabrics of Viscose and Cotton—a new shade card which illustrates a large variety of shades on piece goods, showing equal shade on both fibers. Shade Card I. G. 1101.

Fast Golden Orange Salt G R—another important stable diazo salt added to the already long list which have been placed on the market by General. It produces on Naphtol AS, AS-D, AS-SW, AS-E and AS-TR valuable shades of clear yellow orange which are said to be outstanding in light and general fastness properties. Circular I. G. 1129.

Celliton and Celliton Fast Dyestuffs on Acetate Silk—a sample card illustrating General's 45 Celliton and Celliton Fast dyestuffs on acetate in light and dark shades on piece goods. The card also contains a detailed survey of all the fastness properties of these colors. Sample Card G. D. C. 123.

CLASSIFIED

The rate for "Position Wanted" advertisements in this column is 2 cents a word—with a minimum of 50 cents per insertion. For all other types of advertisements—i.e., help wanted, machinery or supplies for sale—the rate is $5.00 per column inch or less per insertion.

WANTED: Chemist, recent college graduate with one or two years experience or experienced during school vacations in a textile bleaching, finishing or printing plant. State age, height, weight, salary desired, training and experience. Send photograph. P. O. Box 1576, Charlotte, N. C.

WANTED: Salesman wanted by dyestuffs company to cover woolen and worsted mills. Write Box No. 904, American Dyestuff Reporter, 440 Fourth Ave., New York, N. Y.

WANTED: A large manufacturer of chemicals serving the textile industry wishes a chemist who is familiar with the manufacture of Sulphonated Oils and Fats, Emulsions and Sizes. Our laboratory force is informed of this advertisement. All replies treated strictly confidential. Write Box No. 905, American Dyestuff Reporter, 440 Fourth Ave., New York, N. Y.

WANTED: A large manufacturer of chemicals for textiles, requires a salesman with technical and practical experience in finishing Silk, Rayon and Cotton piece-goods. Our sales force is advised of this advertisement. All replies held strictly confidential. Write Box No. 906, American Dyestuff Reporter, 440 Fourth Ave., New York, N. Y.

A REAL OPPORTUNITY FOR THE RIGHT MAN
See page XX